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# REPORT

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Investigation of ..... PHOTOEMISSIVE SURFACES

Subject of Report ..... Part II of Final Report.  
Preparation, Chemical Composition,  
and Properties of Infrared-Sensitive  
Ag-O-Cs Photocathodes.

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## FOREWORD

We wish to acknowledge the assistance of Robert O. Leach who was employed part time during the course of the contract period and who contributed especially to the work described in Section 3.1. Section 1.1 of the report was written by Dr. Khi-Buey Tsai. We also wish to acknowledge our indebtedness to Mrs. Justina Epp of the department of German for her excellent translations of the Russian articles referred to in the subsequent portions of this report. References 1, 24 and 32 of the bibliography were translated by Mrs. Epp. The assistance of George M. Begun with the work of Section 3.2 is also acknowledged.



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## PHOTOCATHODIC SURFACES

### Part II of Final Report.

#### SUMMARY: ORGANIZATION OF REPORT

The present report constitutes Part II of a comprehensive final report on the infrared-sensitive Ag-O-Cs photocathode. The initial step in the preparation of such a photocathode involves oxidation of the silver base in a glow discharge. The technique of oxidation and the products formed have been discussed in Part I. The present report deals, therefore, with the subsequent processing steps and with investigation of the finished photocathode.

A brief description of the manner in which the experiments developed has already been given in the introduction to Part I and need not be repeated here. In view, however, of the length of the present Part (II) it seems advisable for the sake of clarity to state the objectives of the research and to indicate the manner of organization of this report. Some of the most important results are also mentioned in the remainder of the introduction.

In the literature on infrared-sensitive photocathodes there is a notable variability of spectral responses of phototubes prepared by different investigators. We also have had difficulty in reproducibility preparing photocathodes. Because of this experience a systematic study of the process of preparation has been undertaken. Emphasis has been placed on the investigation of chemical changes which occur during the various stages of preparation. In order to make progress it has been necessary to concentrate on the chemical aspect of the problem to the exclusion of such questions as particle size and size distribution. Some qualitative information on particle sizes has been obtained, not sufficient, however, to provide a detailed picture.

Several types of information on chemical composition have been obtained. The amount of oxygen deposited during silver oxidation was measured by means of measuring the change in oxygen pressure. The total cesium entering the phototube envelope was measured with some accuracy by employing capillaries of known dimensions to limit the flow of cesium vapor. The amount of cesium on the cathode was measured using a radioactive cesium tracer. The solid phases in the photocathode were studied by means of x-ray powder diffraction photographs of powder samples scraped,



in vacuo, from the photocathode. Finally, the amount of cesium deposited on glass was determined by measuring the radioactivity of a glass disc, of exactly the same size as the cathode, which was placed at the back of the cathode during fabrication. The combination of all these measurements provides a fairly complete picture of the distribution of cesium in a phototube.

Three main series of experimental studies were carried out. In one of these the thermionic and photoelectric emissions were followed continuously as cesium was added through a fine capillary to a photocathode oxidized to an accurately known extent. No radioactive cesium tracer was employed in these experiments and no x-ray study was performed on the photocathode. In order to minimize the reaction of cesium with glass a comparatively large ratio of cathode area to tube area was used. In some experiments of this series, cesium was permitted to flow without interruption, the thermionic and photoelectric emissions being measured either continuously or at intervals. In other experiments the cesium flow was halted at certain stages and the thermionic and photoelectric emissions were followed with the tube maintained at temperature. Three temperatures were studied, 190°C, 150°C, and room temperature. From these experiments it was found that the reaction by which cesium affects thermionic and photoelectric emission is slow even at 190°C and has a negligibly small rate at room temperature. Utilizing the work of others in conjunction with our own, it is inferred that the slow step is not that which removes cesium from the vapor phase but is a subsequent solid phase transformation. Once a stable infrared-sensitive photocathode is formed the photoelectric yield goes up as the temperature decreases. Very slight excesses of cesium greatly reduce photoelectric yield in the infrared. Numerous other facts of considerable practical interest have also been established as indicated in subsequent sections of the report.

In the second of the three series of experiments, mentioned in the preceding paragraph, the cathode composition was determined using a radioactive cesium tracer. The accurate determination of cathode activity by means of a Geiger counter, required the use of a small cathode of accurately reproducible area. Hence the ratio of cathode area to tube area was considerably smaller than in the experiments of the first series and a larger proportion of cesium reacted with the tube envelope. Cesium flow was also limited by a capillary in most of the experiments and both thermionic and photoelectric emission were followed during the intermediate stages. Cathode composition could not be continuously

followed, however, but was determined only at the end. Photocathodes which were continued only to maximum photoelectric emission were found to contain variable amounts of cesium relative to oxygen, the ratio of the number of cesium atoms to oxygen atoms ( $Cs/O$ ) being considerably less than 2. It was also found at 190°C that when ( $Cs/O$ ) exceeds 2 on the cathode a volatile oxide of cesium is formed which reacts either with the glass wall of the tube or with some other tube element. The introduction of even large excesses of cesium into the tube did not increase the cathode ratio ( $Cs/O$ ) above 2 and in fact caused this ratio to fall well below 2. This fact has practical importance because in some preparative methods rather large excesses of cesium are initially added and subsequently removed either by pumping or by means of a "Cesium Getter". This results in the removal of both cesium and oxygen from the photocathode. Because the cathode reactions are slow, too rapid addition of cesium can result in the pile-up of cesium at the interface, thus producing a local excess and resulting in the formation of a volatile compound. Other results are discussed in subsequent sections.

The third series of experiments involved an x-ray study of the photocathode. A different tube design was again used to facilitate collecting the x-ray powder sample in vacuo. Cesium was again introduced through a capillary and both thermionic and photoelectric emission were followed. Photocathodes carried to maximum photoelectric emission were found to contain  $Cs_2O$  and  $Ag$ . Although no other solids were detected by x-ray analysis in these tubes (maximum photoelectric emission), it is known from the tracer studies that another oxide is present, either unreduced silver oxide or a higher oxide of cesium ( $Cs_2O_3$ ?) or both. The proportion was too low to detect by x-ray diffraction, however. X-ray diffraction studies were also carried out on tubes deficient in cesium and on others containing a considerable excess of cesium. In the cesium-deficient tubes, unreduced silver oxide and  $Cs_2O_3$  were found as well as  $Cs_2O$ . The tubes containing excess cesium were of particular interest for the following reason. In the first series of experiments it was found that when cesium was added without interruption the photoelectric emission passed through a maximum at ( $Cs/O$ )=1.7 and then decreased until at ( $Cs/O$ )=2 and beyond the infrared sensitivity was very small. If, however, the addition of cesium was discontinued well beyond ( $Cs/O$ )=2 and the tube was baked for a considerable period the infrared sensitivity could be largely recovered. This might be due either to the fact that  $Cs_3O$  is an infrared emitter or

to the fact that slow reaction with the glass envelope removed enough cesium (as a volatile oxide) to restore the cathode composition to  $\text{Cs}_2\text{O}$ . It was important, therefore, to prepare a tube for x-ray analysis which could be baked for a reasonable period of time and which contained, after baking, the compound  $\text{Cs}_3\text{O}$ . By careful cleaning of the tube envelope before fabrication this was finally accomplished. The presence of both  $\text{Cs}_2\text{O}$  and  $\text{Cs}_3\text{O}$  was established from the x-ray diffraction photographs for a tube with  $(\text{Cs}/\text{O})=2.8$ . This tube had, however, no infrared sensitivity at the time the x-ray sample was taken, although it passed through an intermediate stage of high (i.e. "normal") infrared sensitivity before an excess of cesium had been added. Since the manner of preparation was such that  $\text{Cs}_3\text{O}$  constituted the outer layer (i.e. the layer at the cathode-vacuum interface), this conclusively establishes that  $\text{Cs}_3\text{O}$  is not an infrared emitter. All evidence from x-ray diffraction, radioactive cesium tracer studies, and gross composition studies points to crystalline  $\text{Cs}_2\text{O}$  (probably containing traces of impurity, i.e. either impurity centers or F-centers) as the infrared emitter. These and other results are discussed in subsequent sections.

In addition to the three series of systematic experiments, briefly mentioned above, other experiments of an exploratory and somewhat fragmentary nature have been carried out partly to develop the technique of photocathode preparation and partly to answer questions of a practical nature which arose during the course of the research. These experiments usually involved the preparation of phototubes by means of a process of a standard sort with one or more variations. Many of these were carried out prior to the three systematic experimental series and were frequently not well understood at the time the experiments were performed. The results have been included in progress reports, sometimes without interpretation and on occasion with interpretation which in hind sight seems erroneous. In order to set the record straight the results of a number of these experiments are also discussed in considerable detail in the light of our present knowledge. In the majority of cases the results are readily understandable and the major inconsistencies are removed. In other cases, however, unanswered questions remain which require further investigation.

The above explanation indicates the manner in which the experiments have been conducted. The organization of the report can best be indicated by discussing briefly the contents of each section.

Section 1 of the report is devoted primarily to a review of the previous work of other investigators on the photocathode. This review is not comprehensive. Only those few papers which we have found particularly helpful are discussed. Section 1.1 contains a review of the chemistry of the cesium oxides. This section was written by Dr. Khi-Ruey Tsai and contains a review not only of previous work but also of some results obtained by him during the course of an x-ray study of  $\text{Cs}_2\text{O}$  and  $\text{Cs}_3\text{O}$  (see Parts III and IV (of this final report series) for an account of the structural study). X-ray powder diffraction spectra are given, where known, for the oxides of cesium, and a summary of their physical and chemical properties is also included. The x-ray powder diffraction spectra are essential for the identification of solid phases in the photocathode and are subsequently used for this purpose (see Section 4). General properties of the oxides are discussed as well as certain specific properties which are of particular interest in photocathode preparation. Section 1.2 is largely historical, the purpose being to provide references to the original works in which important contributions are made to the art of photocathode fabrication. Section 1.3 contains a review of previous work on the determination of photocathode composition. This is followed by a brief summary which outlines the status of the problem at the beginning of the present work. Sections 1.4, 1.5 and 1.6 contain a review of some previous work which must be taken into account in any proposed mechanism for the photoelectric effect in these cathodes. Some work is also reviewed in Section 1.4 which indicates the role of silver in influencing photosensitivity. In some instances we have studied further the phenomena reviewed in these sections but in others we have not, so the material is in considerable measure supplementary to the present research and is included for the sake of providing a complete picture rather than as background to our own work. Several of the researches described are so thorough that there seemed to be no point to extending or repeating them.

For convenience of reference all of the experimental techniques used in the present research are described in Section 2. This avoids the necessity for repetition in the description of experiments in subsequent sections. (There is some unavoidable overlapping between this Section and the experimental section of Part I.) In Section 2 the equipment used is described in some detail. Moreover, complete details of the tube designs and all steps used in the fabrication of each type of experimental phototube are given. Experimental details of the x-ray methods

used in identifying solid phases in the photocathode are given and the techniques of sample preparation are discussed. The calibration of capillaries for limiting cesium flow rate is also discussed. In general the experimental techniques are treated in considerable detail.

In Section 3 the development of thermionic and photoelectric emission during cesium addition is discussed. Selected examples of experimental data are given to illustrate the behavior of both thermionic and photoelectric emission at various chemical compositions. The effect of adding excess cesium at room temperature is pointed out and the changes accompanying heat treatment at various temperatures are described. Phototubes prepared in such a way as to contain  $\text{Cs}_2\text{O}$  are described. The influence of the silver base on photoelectric and thermionic emission is pointed out, with supporting experimental evidence. Much of this Section is devoted to reporting factual information which has been established to be of general validity. The results are interpreted in chemical terms where possible.

In Section 4 the results of cathode composition studies by x-ray analysis and by radioactive cesium tracer analysis are discussed.

In Section 5 the probable mechanism of photoelectric emission is discussed insofar as possible in the present state of development.

## 1. REVIEW OF PREVIOUS WORK

- 1.1 Chemistry of the Cesium-Oxygen System
- 1.2 Preparation of Ag-O-Cs Photocathodes
- 1.3 Composition of Photocathode
- 1.4 Role of Silver in Photocathode
  - 1.41 Photosurface Classification
  - 1.42 Effect of Silver Addition
  - 1.43 Effect of Silver Base on Cathode
- 1.5 Role of Cesium Oxide in Photocathode
- 1.6 Optical Properties of Photocathodes
- 1.7 Structural Studies of Photocathodes
- 1.8 Miscellaneous Experiments
- 1.9 Discussion

## 1. REVIEW OF PREVIOUS WORK

As stated earlier, the following review is not comprehensive. Those papers which provide necessary background for the present work are included and a few others which are of particular importance in indicating the mechanism of photoelectric emission are also included. We are indebted to Dr. Khi-Ruey Tsai for writing Section 1.1.

Some attempt has been made to evaluate the work in terms of our own experience with the photocathode. This is admittedly incomplete since the process of photoelectric emission is still not completely understood. A serious obstacle to a coordinated review is the vagueness shown by many authors in describing the preparation of photocathodes. There is no assurance that the photocathodes studied by different workers are comparable. This makes it difficult, or impossible, to arrive at general conclusions. In several instances excesses of cesium beyond  $\text{Cs}_2\text{O}$  are reported although usually without accurately stating the analytical method used in determining the excess. Our own experiments strongly indicate that an excess of cesium in the cathode results in a marked reduction in infrared sensitivity. Despite these difficulties a number of cathodes have been thoroughly studied and the results are of considerable interest.

### 1.1 The Chemistry of the Cesium-Oxygen System (Khi-Ruey Tsai)

The binary system of cesium and oxygen ranks perhaps only next in complexity to the alkali-sulphur systems. Altogether nine compounds have been reported namely, four suboxides,  $\text{Cs}_7\text{O}$ ,  $\text{Cs}_4\text{O}$ ,  $\text{Cs}_7\text{O}_2$ ,  $\text{Cs}_3\text{O}$ ; one normal oxide,  $\text{Cs}_2\text{O}$ ; three higher oxides,  $\text{Cs}_2\text{O}_2$ ,  $\text{Cs}_2\text{O}_3$ ,  $\text{CsO}_2$ ; and one 'ozonate',  $\text{CsO}_3$ . (See Tables I and II.)

#### Cesium Suboxides $\text{Cs}_7\text{O}$ , $\text{Cs}_4\text{O}$ , $\text{Cs}_7\text{O}_2$ , $\text{Cs}_3\text{O}$

The existence of the four suboxides of cesium was first discovered by Rengade<sup>10</sup> through study of the temperature-composition diagrams (Fig. 1). A part of the phase diagram, ranging from pure cesium to  $\text{CsO}_{0.25}$ , has recently been



TABLE I. PHYSICAL PROPERTIES OF CESIUM SUBOXIDES

Formula	Cs <sub>2</sub> O	Cs <sub>4</sub> O	Cs <sub>7</sub> O <sub>2</sub>	Cs <sub>3</sub> O
Color	Bronze (1)	Coppery Red (1)	Dark Purple (111)	Dark Green (111)
Melting-Point °C	3°	100°d. 2Cs <sub>4</sub> O=Cs <sub>7</sub> O <sub>2</sub> +Cs	50°d. Cs <sub>7</sub> O <sub>2</sub> =2Cs <sub>3</sub> O+Cs	170°d.(?) (1) 165° (111)
Density, g/cc.			2.65 (30°C) (111)	2.73 (30.2°C) (111)
Electrical Resistivity Ohm-cm $\frac{1}{r} \frac{dr}{dt}$	5.1x10 <sup>-5</sup> (-10°C) 0.0029 (11)	6.2x10 <sup>-5</sup> (-10°C) 0.003 (11)		7.2x10 <sup>-5</sup> (30°C) 9.0025 (111)
Magnetic Susceptibility cgs units per g $\chi$			Weakly Paramagnetic (111)	0.15x10 <sup>-6</sup> (111)
X-Ray Powder Data d/n and Relative Intensity	3.95(5), 3.71(10) 3.53(10), 3.30(10) 3.15(4), 2.71(3) 2.62(9), 2.59(9) 2.47(5), 2.27(4) 2.19(9), etc. at -100°C (11)	2.85(2) 2.56(2) at -100°C (11)	8.2(4), 3.97(10) 3.65(5), 3.22(6) 3.02(4), 2.84(4) 2.71(3), 2.49(1) 2.33(1), 1.97(1) 1.79(1), at 25-30°C (11)	7.62(60), 4.39(10) 3.80(100), 3.37(10) 2.87(15), 2.68(50) 2.54(2), 2.28(10) 2.18(10), 2.10(5) 1.89(15), 1.696(10) (11)
Crystal Structure				D <sub>3</sub> c=7.52A 6h a=8.78A u=0.250

Note: (i) E. Rangade (Ref. 7-10); (ii) V.G. Brauer (Ref. 2); (iii) Present Investigation  
See Part IV of this Final Report Series.



TABLE II. PHYSICAL AND CHEMICAL PROPERTIES  
OF CESIUM OXIDE AND SUPEROXIDES

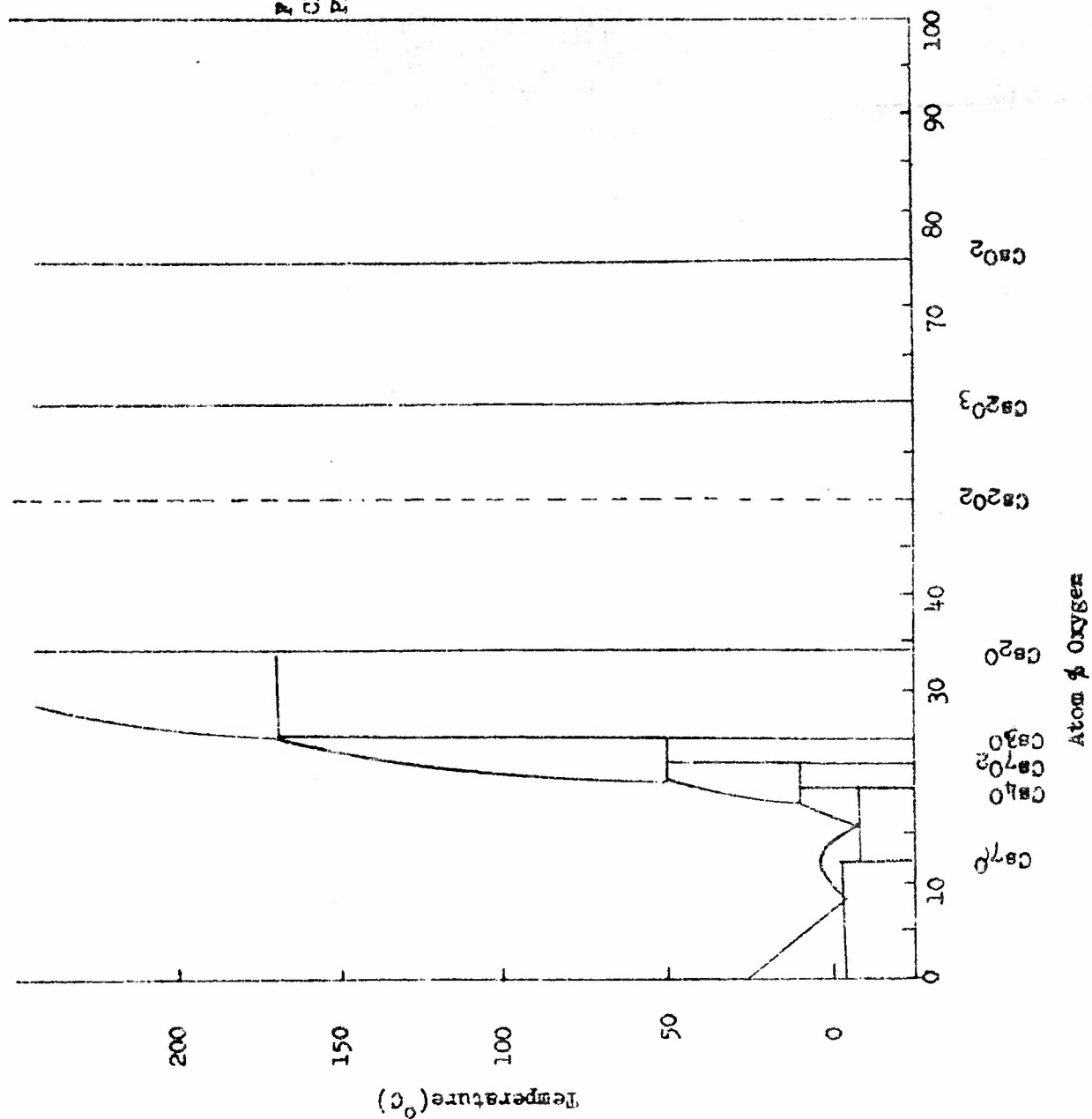
Formula	Cs <sub>2</sub> O	Cs <sub>2</sub> O <sub>2</sub>	Cs <sub>4</sub> O <sub>6</sub> (?)	CsO <sub>2</sub>
Color	Orange	Pale Yellow	Chocolate Brown	Yellow
Melting-Point, °C	350-400°d. (i)	400-450°C (i) 594° (ii)	350-400°d. (i) 502° (ii)	515°(in O <sub>2</sub> atm.) (i) 432° (ii)
Density, g/cc.	4.60 (iii)	4.47(15°)(i)	4.25(0°)(i)	3.68(0°)(i)
Heat of Formation	82.7 Kcal/mol (i)	120.5 Kcal/mol (ii)	2x126 Kcal/mol (ii)	0.5x141 Kcal/mol (ii)
Magnetic Susceptibility	-0.20x10 <sup>-6</sup> cgs per g. (iii)	Diamagnetic (?)	Paramagnetic (?)	9.3x10 <sup>-6</sup> cgs per g. (20°C) (iii)
X-ray Powder Data d/n and Relative Intensity	6.33(5), 3.43(100), 3.80(5) 3.16(25), 2.91(100), 3.60(2) 2.64(1), 2.18(3), 3.06(2) 2.124(25), 1.995(20), 2.60(3) 1.808(10), 1.766(20), 2.44(1) 1.717(10), 1.688(10), 1.92(1) 1.580(5), 1.559(2), 1.88(1) 1.497(1), 1.457(10), 1.62(1) etc. (iv)	4.03(3), 3.49(5) 3.12(10), 2.64(8) 2.47(1), 2.106(4) 2.016(2), 1.937(8) 1.804(4), 1.603(2) 1.563(1), 1.503(3) 1.455(1), 1.426(1) 1.396(1), 1.343(4)	3.82(10), 3.62(8) 3.14(10), 2.39(8) 2.22(6), 2.14(6) 1.925(6), 1.895(5) 1.820(2), 1.616(4) 1.537(5), 1.447(4) 1.419(2), 1.388(2) 1.316(3), 1.111	

TABLE II. (Continued)

Formula	Cs <sub>2</sub> O	Cs <sub>2</sub> O <sub>2</sub>	Cs <sub>4</sub> O <sub>6</sub> (?)	CsO <sub>2</sub>
Crystal Structure	Anti-CdCl <sub>2</sub> (D <sub>3d</sub> ) a=4.256Å c=18.99Å u=0.256		Tn <sub>4</sub> P <sub>3</sub> , R <sub>d</sub> <sup>6</sup> (?) a=9.86Å	CaC <sub>2</sub> -type a=6.28Å c=7.24Å
Thermal Decomposition	2Cs <sub>2</sub> O $\xrightarrow{400^\circ}$ 2Cs <sub>2</sub> O <sub>2</sub> (?) + Cs (i)	2Cs <sub>2</sub> O <sub>2</sub> (?) $\xrightarrow{650^\circ}$ Cs <sub>4</sub> O <sub>6</sub> $\xrightarrow{350^\circ}$ 2Cs <sub>2</sub> O <sub>2</sub> (?) + O <sub>2</sub> (i)		CsO <sub>2</sub> (S) $\xrightarrow{150^\circ}$ Cs <sub>2</sub> O <sub>2</sub> (?) + O <sub>2</sub> (i)
Reaction with Oxygen	Cs <sub>2</sub> O <sub>2</sub> (?) Cs <sub>4</sub> O <sub>6</sub> (?), CsO <sub>2</sub> (i)	Cs <sub>4</sub> O <sub>6</sub> (?), CsO <sub>2</sub> CsO <sub>2</sub> (i)		No Reaction
Reaction with Cesium	Dissolves slowly to form suboxide	Decomposed by cesium at 170°C		CsO <sub>2</sub> $\xrightarrow{170^\circ \text{ Cs}}$ Cs <sub>2</sub> O + suboxides (iv)
Reaction with Water	Cs <sub>2</sub> O + H <sub>2</sub> O $\rightarrow$ 2CsOH (i)	Cs <sub>2</sub> O <sub>2</sub> + 2H <sub>2</sub> O $\rightarrow$ 2CsOH + H <sub>2</sub> O <sub>2</sub> (i)	Cs <sub>4</sub> O <sub>6</sub> (?) + H <sub>2</sub> O $\rightarrow$ CsOH + H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub> (i)	2CsO <sub>2</sub> + 2H <sub>2</sub> O $\rightarrow$ 2CsOH + H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub> (i)

Note: (i) E. Rengade (see Ref. 7-10); (ii) Centnerswer and Blumenthal (see Ref. 3); (iii) Helms and Klemm (see Ref. 4-6); (iv) Present Investigation. See Part III of this Final Report Series.

FIG. 1  
CESIUM-OXYGEN  
PHASE DIAGRAM



substantiated by Brauer<sup>2</sup> by means of x-ray diffraction powder diagrams and measurement of the resistivity-temperature coefficients of the suboxide system at various compositions.

The usual way of preparing cesium suboxides is by direct combination of pure cesium with the calculated amount of pure oxygen admitted in small portions. This works smoothly with the lower-melting suboxides. In the case of the higher-melting suboxides,  $\text{Cs}_7\text{O}_2$  and  $\text{Cs}_3\text{O}$ , however, it becomes necessary, according to our experiments, to conduct the oxidation in the presence of a small amount of inert gas (argon); this prevents excessive volatilization of the alkali metal at the higher reaction temperature necessary for maintaining the reaction products in the molten state. Crystalline  $\text{Cs}_3\text{O}$  can also be prepared by distilling a lower suboxide ( $\text{Cs}_7\text{O}_2$ ) in a pyrex capillary at 120 - 130°C, although some  $\text{Cs}_2\text{O}$  (yellowish film on top of the dark-greenish  $\text{Cs}_3\text{O}$  crystals) is also formed in this process, indicating that  $\text{Cs}_3\text{O}$  has appreciable dissociation pressure at 120 - 130°C.

The physical properties of the cesium suboxides are summarized in Table I. It is interesting to note that all the suboxides of cesium exhibit metallic properties. Many attempts to get a good powder pattern of the suboxide,  $\text{Cs}_7\text{O}_2$ , have failed because of the difficulty to identify and eliminate any foreign phases. The powder lines shown in Table I are those which consistently appeared in samples of the suboxide. There were weak lines at  $d/n = 6.4, 5.8, 5.3, 5.0, 4.7, 4.3, 4.1$  from one sample but not from the other. These might be superlattice lines or lines due to higher oxides. According to x-ray single-crystal and powder data obtained in this laboratory,  $\text{Cs}_3\text{O}$  has a  $D_{6h}$  ( $C_6/mcm$ ) structure, with two molecules per unit-cell, in which the Cs-O has an ionic bond distance (2.89Å as compared with Cs-O = 2.86Å in  $\text{Cs}_2\text{O}$  crystal) and the Cs-Cs has a metallic bond distance (5.80Å as compared with Cs-Cs = 5.36Å in metallic cesium). Probably all the suboxides of cesium possess partial metallic structures as indicated by their metallic properties. It is to be noted that silver subfluoride,  $\text{Ag}_2\text{F}$  (anti- $\text{CdI}_2$  structure), has also been found<sup>11</sup> to possess metallic properties and partial metallic structure in which the Ag-F distance is about the same as that in silver fluoride,  $\text{AgF}$ , crystals and the Ag-Ag distance the same as that in metallic silver. Thus the metal suboxides and subhalides probably belong to the same class as far as structural chemistry is concerned.

It has not been established whether  $\text{Cs}_2\text{O}$  has a true melting-point or peritectic temperature around  $165^\circ\text{C}$ , nor whether it forms a limited range of solid solution with  $\text{Cs}_2\text{O}$ . However, according to the x-ray powder diagrams of partially oxidized  $\text{Cs}_3\text{O}$ , of dark-colored  $\text{Cs}_2\text{O}$  known to contain a slight excess of cesium, and of a binary system corresponding to the composition  $\text{Cs}_{2.5}\text{O}$ , no other suboxides appear to exist in the composition range between  $\text{Cs}_3\text{O}$  and  $\text{Cs}_2\text{O}$ .

By heating above their melting-point or peritectic temperatures, all the suboxides of cesium appear to be converted into solutions of cesium monoxide in liquid cesium, the color of the melt varying from yellow to orange to dark red as the oxygen content or the  $\text{Cs}_2\text{O}$  concentration increases. By maintaining the temperature above  $180^\circ\text{C}$ , all the excess cesium can be distilled off and agglomerates of laminated red crystals of  $\text{Cs}_2\text{O}$  are left behind.

The suboxides of cesium are decomposed by water to form cesium hydroxide with evolution of hydrogen; thus chemically they react like a mixture of  $\text{Cs}_2\text{O}$  and metallic cesium.

#### Cesium Monoxide, $\text{Cs}_2\text{O}$ .

Orange crystals of  $\text{Cs}_2\text{O}$  can be conveniently prepared by distilling off the excess cesium from a lower suboxide ( $\text{Cs}_3\text{O}$ ) in a pyrex tube at  $180 - 200^\circ\text{C}$ . The distillation usually takes about two days, the last traces of excess cesium coming off very slowly.

Attempts to prepare  $\text{Cs}_2\text{O}$  by direct combination of equivalent amounts of pure cesium and oxygen have failed owing to the high melting-point of the desired product and the tendency to form a surface coating of high-melting higher oxides of cesium.

Oxidation of a dilute cesium amalgam with gaseous oxygen leads to the formation of dark-colored, complicated reaction products containing divalent mercury.

According to Borziak<sup>1</sup>, a yellow film having the composition of  $\text{Cs}_2\text{O}$ , with pronounced photoelectric sensitivity, can be obtained by treating a transparent to whitish  $\text{CsO}_2$  film with cesium vapor at  $150 - 180^\circ\text{C}$ .

Continued exposure of this yellow ' $\text{Cs}_2\text{O}$ ' film to a little more cesium vapor at  $200^\circ\text{C}$  transforms it into a red ' $\text{Cs}_2\text{O}$ ' film with much lower photoelectric sensitivity.

At room temperature, cesium monoxide exists as orange, laminated plates with more or less perfect basal cleavage, soft and friable, easily pulverized by shaking with glass beads. It has an anti- $\text{CdCl}_2$  layer structure<sup>7</sup> in which the charge distributions of the cesium ions appear to be highly polarized.

At the temperature of dry ice acetone, the color of the monoxide becomes pale yellow, there being no change in the structure as shown by the low-temperature x-ray powder diagram obtained in this laboratory. When heated above  $180 - 200^\circ\text{C}$ , the monoxide becomes dark red. According to Rengade<sup>7,8</sup>, it turns black at  $250^\circ\text{C}$ , and is slightly volatile at this temperature. The monoxide also becomes darkened on exposure to cesium vapor at room temperature.

Brauer<sup>2</sup> reported that the outermost layer of the monoxide readily changed to dark brown and dirty tan during storage in a closed tube, and that color changes could also be brought about by irradiation with sunlight or x-rays, or even by mechanical agitation. However, this was not substantiated by our experiments.

According to Rengade<sup>7,8</sup>, cesium monoxide melts at  $350 - 400^\circ\text{C}$  with decomposition into a higher oxide ( $\text{Cs}_2\text{O}_2$ ?) and cesium vapor (?); it reacts with hydrogen at  $160 - 180^\circ\text{C}$  to form  $\text{CsOH}$  and  $\text{CsH}$ ; with oxygen at  $170^\circ\text{C}$  to form a mixture of higher oxides; and with molten sulphur to form a mixture of sulfate, sulfide or polysulfide. The monoxide reacts violently with water to form the hydroxide, and with liquid ammonia slowly to form a mixture of amide and hydroxide. In contact with oxygen at room temperature, the orange powder of cesium monoxide rapidly becomes dirty tan according to our experiments; but further absorption of oxygen appears to be slow, although on prolonged exposure to oxygen a thin layer of  $\text{Cs}_2\text{O}$  can be converted into the yellow  $\text{CsO}_2$ .

#### Cesium Peroxide, $\text{Cs}_2\text{O}_2$

Impure cesium peroxide containing small amounts of amide and hydroxide has been prepared by Rengade<sup>8</sup> by the oxidation of cesium in liquid ammonia with the calculated

amount of oxygen. It has also been prepared<sup>8,3</sup> by direct combination of cesium and oxygen followed by rapid fusion of the reaction mixture in an aluminum vessel; however, the molten oxide and peroxides of cesium have been found<sup>8</sup> to attack all glass and metal containers vigorously. According to Rengade<sup>8</sup>,  $\text{Cs}_2\text{O}_2$  is pinkish to pale yellow, melts at  $400 - 450^\circ\text{C}$  into a dark colored liquid, and reacts with water to give  $\text{CsOH}$  and  $\text{H}_2\text{O}_2(?)$ . However, Centnerswer and Blumenthal<sup>3</sup> gave the melting-point of the peroxide as  $594^\circ\text{C}$ .

No x-ray data for this peroxide have been recorded in the literature. However, the extra powder lines from partially oxidized  $\text{Cs}_2\text{O}$  powder samples prepared in this laboratory (see report on the structure of  $\text{Cs}_2\text{O}$ , Part III of this final report) strongly suggest the presence of this peroxide as a principal oxidation product when cesium monoxide is exposed to a limited amount of oxygen.

#### Cesium Sesquioxide, $\text{Cs}_2\text{O}_3(?)$

The dark brown cesium sesquioxide,  $\text{Cs}_2\text{O}_3(?)$ , appears to exist as an intermediate oxidation product when a solution of cesium in liquid ammonia is treated with oxygen<sup>8</sup>. According to Centnerswer and Blumenthal<sup>3</sup>, the existence of the sesquioxide is indicated by the oxygen dissociation pressure of a sample prepared by prolonged oxidation of cesium with the requisite amount of oxygen. However, most of the dissociation pressure data appeared to be taken above a molten phase; furthermore, they also reported the dissociation pressure of potassium sesquioxide,  $\text{K}_2\text{O}_3(?)$ , the existence of which was not substantiated by x-ray analysis<sup>6</sup>.

Nonstoichiometric samples of the sesquioxide ( $\text{CsO}_{1.38}$ ,  $\text{CsO}_{1.4}$ ) have been prepared by Helms and Klemm<sup>6</sup> by the oxidation of cesium monoxide with oxygen at  $200^\circ\text{C}$ . The same investigators reported that the absorption of oxygen by cesium monoxide appeared to be slow below  $150^\circ\text{C}$ . On further heating to about  $200^\circ\text{C}$ , the absorption became vigorous with evolution of heat and local glowing and melting. However, the absorption of oxygen stopped at about  $\text{CsO}_{1.4}$ . Attempts by the same investigators<sup>6</sup> to prepare the sesquioxide by direct combination of cesium and oxygen were unsuccessful because of incomplete reaction. A dark brown sample of approximate composition  $\text{CsO}_{1.4}$  was prepared in this laboratory by direct combination of the elements. The difficulty of obtaining a stoichiometric product seems to arise from the premature caking of the reaction mixture caused by the formation of an



impervious crust of the higher oxides,  $\text{Cs}_2\text{O}_3(?)$  or  $\text{CsO}_2$ , which prevents further oxidation of the occluded lower oxides. Rapid fusion of the incomplete reaction product in the remaining oxygen fails to increase the oxygen absorption, probably because of the low rate of diffusion of the oxygen through a molten layer of the lighter, higher oxides.

According to Helms and Klemm<sup>6</sup>, x-ray powder data indicate a  $\text{Th}_2\text{P}_3$  structure ( $\text{T}_9$ ) for both cesium and rubidium sesquioxides. Hence the two sesquioxides probably should be written as  $\text{Cs}_4(\text{O}_2)_3$  and  $\text{Rb}_4(\text{O}_2)_3$ ; the three  $\text{O}_2$ -groups probably exist as  $2\text{O}_2^{\cdot-}$  and  $\text{O}_2^{\cdot-}$ ; the dark color of the sesquioxides can be ascribed to the sharing of one set of lattice sites by the  $\text{O}_2^{\cdot-}$  and  $\text{O}_2^{\cdot-}$  ions. However, the structure can not be regarded as being established since the x-ray powder data were taken with nonstoichiometric samples,  $\text{CsO}_{1.4}$  and  $\text{RbO}_{1.4}$ .

#### Cesium Superoxide, $\text{CsO}_2$

Cesium superoxide,  $\text{CsO}_2$ , can be prepared by prolonged oxidation of cesium in liquid ammonia with excess oxygen<sup>8,5</sup>. The yellow superoxide is also obtained when cesium vapor is allowed to diffuse into excess oxygen (see Part III of this final report series, on the preparation, properties, and structure of  $\text{Cs}_2\text{O}$ ), or when a thin film of cesium, or lower oxides of cesium, is exposed to excess oxygen over a prolonged period at room temperature. The superoxide begins to lose oxygen at  $350^\circ\text{C}$ .

The presence of the superoxide ion<sup>5</sup>,  $\text{O}_2^{\cdot-}$ , in the crystal is indicated by the  $\text{CaC}_2$ -type structure, by the observed paramagnetic susceptibility, and by the analogy with potassium and rubidium superoxides,  $\text{KO}_2$  and  $\text{RbO}_2$ . Cesium superoxide is expected to be a colored compound because of the presence of an unpaired electron in the  $\text{O}_2^{\cdot-}$  ion. However, a sufficiently thin film of the yellow superoxide might appear to be colorless<sup>1</sup>.

The physical and chemical properties of the monoxide and higher oxides of cesium are summarized in Table II. The peroxide,  $\text{Cs}_2\text{O}_2$ , appears to be the most stable of the four compounds at higher temperature, whereas at room temperature  $\text{Cs}_2\text{O}$ ,  $\text{Cs}_2\text{O}_2$ , and  $\text{Cs}_2\text{O}_3(?)$  are all unstable towards oxygen. The peroxides are, however, unstable towards cesium vapors, although the reaction appears to be very slow at room temperature. Thin films of the higher



oxides, formed during the preparation of  $\text{Cs}_3\text{O}$  (see Part III of this final report series), gradually turned red upon continued exposure to cesium vapor; and when a small amount of the yellow superoxide was digested with a molten suboxide ( $\text{Cs}_7\text{O}_2$  or  $\text{Cs}_3\text{O}$ ) at  $150 - 170^\circ\text{C}$ , the superoxide was readily decomposed. The monoxide,  $\text{Cs}_2\text{O}$ , itself also dissolves slowly in excess cesium to form the suboxide. It remains to be established, however, whether  $\text{Cs}_2\text{O}_2$  and  $\text{Cs}_2\text{O}_3(?)$  can be obtained from  $\text{CsO}_2$  by the addition of cesium. Otherwise the whole range of the phase diagram from Cs to  $\text{CsO}_2$  can be regarded as reversible in the sense that under suitable conditions a higher oxide can be obtained from a lower oxide by the addition of oxygen, and a lower oxide can be obtained from a higher oxide or peroxide by the addition of cesium.

#### Oxidation of Cesium with Silver Oxide

When powdered silver oxide was added to molten cesium (initial composition of the system:  $2\text{Ag}_2\text{O}+7\text{Cs}$ ), a vigorous reaction took place. X-ray powder photographs of the reaction mixture showed Ag lines,  $\text{Cs}_7\text{O}_2$  lines ( $d/n=8.3, 3.9, 3.2, 2.7$ ), but no  $\text{Ag}_2\text{O}$  lines.

When cesium was slowly distilled onto a thin layer of powdered  $\text{Ag}_2\text{O}$ , a thin coating of the higher oxides was soon formed which prevents further reduction of the unchanged  $\text{Ag}_2\text{O}$  by the excess cesium. By digesting the reaction mixture at  $130^\circ\text{C}$  for 8 hours, however, some of the powder lines apparently due to higher oxides of cesium appeared to decrease in intensity. The difficulty of identifying the reaction products with the higher oxides of cesium lies in the fact that the powder patterns of  $\text{Cs}_2\text{O}_2$  and  $\text{Cs}_2\text{O}_3(?)$  have not been definitely established; both compounds might have some powder lines above  $d/n=4.1$ , as the cells are expected to be large.

#### Cesium Ozonate, $\text{CsO}_3$

According to Whaley and Kleinberg<sup>12</sup>, the formation of cesium ozonate when an anhydrous powder sample of cesium hydroxide is heated with ozonized air is indicated by the orange-red color of the sample, the amount of oxygen liberated upon decomposition with water, and the observed paramagnetic susceptibility. The sample when freshly prepared gives no peroxide test; the orange-red product is soluble in liquid ammonia and decomposed at  $170^\circ\text{C}$  into

a mixture of white and yellow solid ( $\text{CsO}_2$ ?) which gives positive peroxide test. However, the ammonia extract appears to contain more than one substance.

## 1.2 Preparation of Ag-O-Cs Photocathodes

Since the original surface development by Koller<sup>13</sup> in 1929, numerous different preparative procedures have been reported leading to surfaces having very different spectral responses and sensitivities. In relationship to investigations described later, two types of preparative procedures are of interest; namely, the massive cathode and the semitransparent cathode surfaces. It is to be noted that the good infrared-sensitive surfaces prepared by the different methods have similar spectral response characteristics and therefore common structure and chemical characteristics.

The massive cathode Ag-O-Cs surface is primarily of interest because of the relative simplicity of preparation. The following procedure is commonly used for the preparation of a massive cathode tube<sup>14</sup>. A massive silver sheet cathode is formed into a semicylindrical shape and is mounted on a wire through a press seal in a glass tube envelope. The anode is formed by a second wire through the press seal. Commonly, a nickel cup containing a pellet formed from a mixture of cesium chromate and silicon is mounted within the tube envelope in such a position as to be readily accessible for induction heating. The tube, being sealed to a vacuum system, is thoroughly outgassed in a high vacuum at an elevated temperature (300 - 400°C). Subsequently, oxygen is introduced into the system to a pressure of the order of 1 mm Hg and the silver is oxidized by a glow discharge. The extent of oxidation is generally controlled by the color of the oxide surface. After oxidation the tube is evacuated to less than  $10^{-5}$  mm Hg, the cesium pellet is fired, and the tube is baked at 180 - 200°C for a period of time. The time of bake may be controlled by observing the color of the cathode or by measuring the thermionic emission. The maximum infrared sensitivity is related to a maximum thermionic emission. At the end of the bake the tube is sealed off. It has been reported that the photosensitivity lost due to excessive baking may be recovered by bombardment of the surface with an argon glow discharge<sup>15</sup>, but spectral response data are not reported.

The semitransparent cathode may be prepared using a variety of procedures to enhance the photosensitivity. The procedure described by Zworykin and Ramberg (see ref. 14,

p. 95) is as follows. The tube consists of a silver bead evaporator unit mounted in a glass tube envelope with a metal photosurface contact lead sealed through the tube wall at the edge of the photosurface area. The periphery of the area on which the photosurface is to be formed is usually coated with a conducting film of gold or platinum which makes contact between the photosurface and the metal lead-in wire. After evacuation and outgassing, a 50 percent transmission silver film is evaporated on the glass surface by electrical heating of the silver bead or wire in the evaporator unit. The surface is then fully oxidized by a glow discharge in oxygen, and a second silver film is evaporated to reduce the transmission to 50%. After heating the evacuated tube to 180 - 200°C, cesium is carefully added from an auxiliary source until a maximum in thermionic emission is observed. At this point the cesium addition is discontinued, and after the surface has developed maximum thermionic emission, the tube is cooled and sealed off. The deposition of the second silver layer is related to the formation of a conducting surface from which thermionic emission may occur<sup>16</sup>.

The sensitivity of the cathode may be increased further after the initial fabrication by the careful evaporation of additional silver or gold on the surface to give a maximum photosensitivity<sup>17</sup>. This process has the net effect of increasing photosensitivity and decreasing thermionic emission without changing the thermionic work function. The phenomena involved are discussed further in the following section.

It is frequently observed that, after fabrication, the spectral response of a tube changes with time at room temperature<sup>18</sup>. Consequently, the tubes are frequently given a stabilizing bake at elevated temperatures (100 - 150°C) for varying periods of time. In later portions of this report this variation in tube characteristics is shown to be related to the equilibration of the gross chemical composition of the tube.

A good review of the methods of preparing photocathodes has been published by Hartmann<sup>18a</sup>.

### 1.3 Photosurface Composition

Since 1929 several experiments have been performed in an effort to establish the composition of the cesium oxide involved in the photosensitivity of the silver-

oxygen-cesium photocathode. Precision was not high in these experiments because of the small quantities involved and the fact that appreciable cesium is deposited on other surfaces than the photocathode.

One of the first composition studies was performed by L.R. Koller<sup>19</sup>. In this investigation the cesium released by firing a  $\text{Cs}_2\text{CrO}_4$ -Si pellet was deposited on a cathode surface and the photoemission of the surface followed during the reaction of this cesium with oxygen introduced at a fixed rate. The composition of the surface was calculated from the amount of oxygen required to reach maximum photosensitivity and assuming a 100% cesium yield from the pellet. From such experiments Koller concluded that the surface consisted of a thin film of cesium on a surface consisting of the suboxides of cesium. Since subsequent experiments have shown that the cesium yield from  $\text{Cs}_2\text{CrO}_4$ -Si pellets is usually less than 100%, these conclusions are not accurately valid. Koller's work is, however, of considerable interest for other reasons.

In 1931 N.R. Campbell<sup>20</sup> reported the results of a rather careful investigation of the photosurface composition. In these experiments the amount of oxygen deposited during the glow discharge oxidation of silver was measured directly by the pressure change in the static system. Cesium obtained by the thermal decomposition of cesium azide was introduced into the tube using a capillary to control the flow rate. The capillary was calibrated by a direct analytical determination of the cesium flow rate per unit time. It was found that the Cs/O ratio for the sensitive surface was 2.0 and Campbell concluded that the oxide was  $\text{Cs}_2\text{O}$ . It is to be noted that these results refer to the quantities of cesium and oxygen in the phototube and not to the amounts on the photocathode itself. Significant quantities of cesium also react with the glass wall of the phototube.

Prescott and Kelly<sup>18</sup> performed an analysis of the photosurface in the following manner. The oxidation was performed by repeated discharge of a high-voltage condenser across the tube. The amount of oxygen deposited per discharge was determined in an auxiliary experiment. After the silver was oxidized to a known extent, the cesium was introduced and the tube fabricated. Microchemical analyses of the tube demonstrated that 68% of the initial cesium was on the cathode and 32% on the inner surfaces of the glass envelope. The initial cesium was recovered to a 3% accuracy.

Assuming that the oxygen deposited during oxidation remained on the cathode, they arrived at the photo-surface composition  $Cs_{2.1}O$  and concluded that the active species was  $Cs_2O$ . They also report that the microanalysis indicated the presence of 0.13 mg of unreacted  $Ag_2O$  on the cathode. This result is surprising considering that the tubes were fabricated at 200 - 225°C. Assuming the oxide was  $Ag_2O$  this would correspond to  $5.38 \times 10^{-7}$  moles of  $Ag_2O$  or the equivalent of 605 condenser discharges. Detailed data are not presented for the tubes which were analyzed; however, it was stated that the most satisfactory surfaces were obtained using approximately 100 discharges. In this experiment the question of the oxidation of tube elements or possible loss of oxygen from the surface was not considered.

In 1946 Sayama reported the results of an investigation of the vapor pressure of the cesium oxide photocathode<sup>21</sup>. The cesium flow rate into the experimental tube was controlled by the rate of effusion of cesium through a hole bored in a platinum plate which was mounted in a side tube. The amount of cesium introduced was calculated using the known vapor pressure of cesium and Knudsen's equation for flow through an orifice. The cesium pressure in the tube was measured with an ionization gauge using Langmuir's method which depends on the fact that a cesium ion is produced in every collision of a cesium atom with a hot tungsten filament. The thermionic emission and white light photo-sensitivity were measured periodically during the cesium addition.

In the experiments it was observed that very shortly after the maximum thermionic emission and white light sensitivity, the vapor pressure of cesium increased very rapidly. Since this was observed at 2.0 (Cs/O), Sayama concluded that during continuous cesium addition the maximum thermionic and photoelectric emissions are associated with the formation of  $Cs_2O$ . At cesium compositions greater than  $Cs_2O$ , Sayama noted that the thermionic and photoelectric emissions returned to their maximal values on cooling the cesium source. This was interpreted as being caused by the effusion of cesium back into the cesium source, and consequently as indicating that the process was fully reversible! It is to be noted that the cesium partial pressure in the tube was not constant during the cesium addition, as would be anticipated if equilibrium had been established during the process of addition. During the cesium addition the partial pressure of cesium was less

than  $1 \times 10^{-10}$  mm Hg for Cs/O  $\leq 1.4$ , approximately  $8 \times 10^{-10}$  mm Hg at Cs/O = 2.0, and increased rapidly beyond 2.0 Cs/O to approximately  $4 \times 10^{-8}$  mm Hg at Cs/O = 2.5. The sudden increase in pressure at Cs/O = 2.0 was regarded as resulting from the deposition of a layer of excess cesium on the surface of Cs<sub>2</sub>O.

Sayama also prepared a series of cathodes with variable composition which were sealed off from the cesium source and given a stabilizing bake. For these tubes the form of the spectral response curves did not vary significantly for  $2 < \text{Cs/O} < 3$ . The absolute yield of the photoelectric and thermionic emissions also remained nearly at the same values for this composition range. Sayama therefore concluded that the greater part of the excess cesium was present as the suboxide, Cs<sub>3</sub>O. (See Section 4 for further discussion of this point.) In addition, Sayama found that in the composition range Cs/O > 2.6 the ion gauge did not behave as expected for pure cesium. He suggests that the results are interpretable on the assumption that cesium oxide molecules, possibly Cs<sub>3</sub>O, are present in the gas phase. Further confirmation for the formation of a volatile compound has been obtained during the course of the present investigation (see Section 4).

Although Sayama concluded that Cs<sub>2</sub>O is the species responsible for photoelectric emission in the infrared, and although our results, to be described later, are compatible with this conclusion, nevertheless we do not believe that his results lead unambiguously to this conclusion. Reaction with the tube envelope is important. This is indicated by the work of Prescott and Kelly and has been confirmed in our work. No correction for this factor was made by Sayama. Moreover, his conclusion that recovery of photoemission on cooling the cesium source to 0°C is due to the diffusion of cesium back from the photocathode to the source is not correct. At a cesium-oxygen ratio of 2.0 the pressure of cesium is below  $10^{-9}$  mm Hg above the photocathode while the equilibrium vapor pressure of cesium is  $10^{-7}$  mm Hg at 0°C. We have found, in addition, that infrared sensitivity increases on cooling a cesium source both before and after the maximum emission (see Section 3).

The published results of Campbell, Prescott and Kelly, and Sayama agree in that Cs<sub>2</sub>O is indicated as the active ingredient. There seems to be some question, however, as to why they should agree since neither Campbell nor Sayama took into account the reaction of cesium with the tube walls, while Prescott and Kelly did take this factor into account. Our own decision to reinvestigate the question arose for



several reasons. The apparent contradiction mentioned above was one reason. Another reason arose during the course of an investigation of semitransparent cathodes prepared in such a manner as to contain  $\text{Cs}_2\text{O}$ . The preparative method was patterned after experiments on bulk quantities of cesium suboxides which showed conclusively that  $\text{Cs}_2\text{O}$  is the end product when a cesium suboxide is heated to  $190^\circ\text{C}$  in vacuo (see Section 1.1). The photocathodes prepared in this way were not, however, highly infrared-sensitive. The composition was therefore reinvestigated in the manner already indicated in the introduction.

#### 1.4 Role of Silver in the Photocathode

We have not systematically studied the influence of silver on the photocathode, although in one instance an important influence of the silver base has been demonstrated conclusively (see Part I of this report series, also Sections 3.51 and 4.12 of the present report). Nevertheless, the distribution of silver in the photocathode has an important influence on photosensitivity and any proposals as to the origin of photoelectrons must take this factor into account. In this section, therefore, some previous work which bears on this matter is reviewed. The work of Asao<sup>23</sup> is summarized in considerable detail both because of its bearing on the role of silver in the photocathode and also because of the important auxiliary experiments which were performed.

##### 1.41 Photosurface classification

De Boer has developed a classification for the photosurfaces formed by the reaction of cesium with oxygen on a silver base. The classification is based in part on the photoelectric response, the conditions of preparation, and a physical model of the photosurface<sup>22</sup>. The classification serves to indicate in a compact way the importance of silver distribution and serves as a useful introduction. The classification data are given in Table III.

The above classification is based on the method of preparation. The methods are so selected, however, as to suggest the distribution of constituents, particularly silver, in the photocathode. The deposition of  $\text{Cs}_2\text{O}$  on a layer of silver does not produce a cathode with as high relative infrared sensitivity as does the addition of cesium to oxidized silver. The latter process no doubt results in

TABLE III. Ag-O-Cs PHOTOSURFACES

Cathode*	Photoelectric Threshold (m $\mu$ )	Longest Wavelength Photoemission Maxima (m $\mu$ )
(Ag)-O,Cs	800	350
(Ag)-Cs <sub>2</sub> O-Cs	~ 1150	610
(Ag)-Cs <sub>2</sub> O, Ag-Cs	~ 1200	700 to 800
(Ag)-Cs <sub>2</sub> O, Ag-Cs with extra Ag(Me)	~ 1200	750 to 800
(Ag)Cs <sub>2</sub> O, Cs, Ag-Cs	to ~ 1400	750 to above 800
(Ag)Cs <sub>2</sub> O, Cs, Ag-Cs with extra Ag(Me)	to ~ 1700	750 to 850

\* The conditions for the preparation of the cathodes were as follows:

(Ag)-O,Cs

Heat a clean silver surface in oxygen at 360°C, cool, evacuate, heat treat at 300°C in the presence of cesium. (Corresponds presumably to thin Cs<sub>2</sub>O layer).

(Ag)-Cs<sub>2</sub>O-Cs

Deposit a thin layer of cesium on silver, oxidize the cesium, treat oxide with cesium. (Corresponds presumably to thick Cs<sub>2</sub>O layer).

(Ag)-Cs<sub>2</sub>O, Ag-Cs

Oxidize silver in a glow discharge, introduce cesium, and react by heating to 250°C. (Corresponds presumably to Ag base with an intermediate layer of Cs<sub>2</sub>O and Ag, and an adsorbed layer of Cs).

(Ag)-Cs<sub>2</sub>O, Ag-Cs  
with extra Ag (Me)

Above surface with silver added by evaporation from an auxiliary source. (Ag layer added to above surface).



TABLE III. (Continued)

\* The conditions for the preparation of the cathodes were as follows:

(Ag)-Cs <sub>2</sub> O, Cs, Ag-Cs	Heat treat (Ag)-Cs <sub>2</sub> O, Ag-Cs surface in excess Cs vapor for some time at 200°C. (Same as (Ag)-Cs <sub>2</sub> O, Ag-Cs but additional Cs introduced into Cs <sub>2</sub> O).
(Ag)-Cs <sub>2</sub> O, Cs, Ag-Cs with extra Ag (Me)	Add Ag to previous surface by evaporation from a source. (Ag layer added to above surface).

a more intimate mixing of silver with  $\text{Cs}_2\text{O}$  in the finished cathode. According to de Boer's model of the photocathode the photoelectrons originate from cesium atoms adsorbed on the surface of  $\text{Cs}_2\text{O}$ . The first cesium atoms to be adsorbed go to "active" spots where the atoms are most firmly bound. On irradiation, photo ionization occurs. The shift in long wave limit for adsorbed cesium atoms as compared with isolated cesium atoms is attributed to the fact that in the former case the positive ion produced is very strongly bound to the lattice surface. (See Fig. 78 of ref. 22 where the case of Cs on  $\text{CaF}_2$  is illustrated. Cs on  $\text{Cs}_2\text{O}$  is presumed to be similar. See also Fig. 86 of ref. 22 where the adsorption of cesium on  $\text{CaF}_2$ ,  $\text{BaF}_2$ , etc. is illustrated.) A distinction has been made by de Boer between photocathodes with thin and thick intermediate layers (i.e.,  $\text{Cs}_2\text{O}$  between metal base and a surface photosensitive layer). In the former case (thin layer) a very high electrostatic field is produced by positive ions formed in photoionization and hence electrons are pulled out of the base metal to replace those removed by photoionization. In the case of thick layers, on the other hand, the electrostatic field at the metal base is reduced because the positive ions at the surface are now further removed from the base. Electrons lost on photoionization are therefore replaced much more slowly when the intermediate layer is thick. This results, according to de Boer, in a photoelectric current which does not reach saturation until very high potentials are applied between cathode and collector plate. In order to increase the conductivity of the intermediate layer it is important that it should be mixed with a finely dispersed metal. When this is done the photoelectric current saturates at much lower collector voltages (see Fig. 134 of ref. 22 for an example in which cesium is added respectively to  $\text{BaF}_2$  and to  $\text{BaF}_2$  mixed with tungsten and barium. Saturation is reached at much lower voltages in the latter case. Cs on  $\text{Cs}_2\text{O}$  is presumably similar.) In accordance with this conception a good deal of work has been done in which photocathodes are prepared in such a way that it might be reasonably assumed that finely dispersed metal is added to the intermediate layer. This might be done by evaporating metals onto the photocathode after preparation by partially reducing the silver oxide before adding cesium, by bombarding a cathode with positive ions in a discharge, etc. Not only silver but also alkali metals, particularly cesium, may be added to the intermediate layer and have a marked influence on the photocathode. One method of adding cesium to the

intermediate layer is to heat a photocathode in cesium vapor at 200°C. It is interesting to note De Boer's statement that this achieves the desired effect much more easily when foreign atoms (e.g. silver) are already present (see page 322 of ref. 22). The examples of Table III provide a summary showing the effect of several methods of preparation designed to add finely dispersed metal or metal atoms to the intermediate layer. The subject is discussed at length with references to the literature in Chapter XIII of de Boer's book. It is of more interest here to discuss in some detail the thorough and systematic study by Asao, of the addition of one constituent (silver) to the photocathode.

#### 1.42 Effect of silver addition

The increase in photo sensitivity caused by evaporating silver onto the photosurface has been extensively studied by Asao<sup>23</sup>. During the course of this work, which is unusually thorough and complete, a considerable amount of fundamental factual information has been established. On this account and because of the intrinsic interest in the effect of added silver this work is reviewed in detail.

The investigation may be conveniently considered in two parts; namely, the evaporation of silver onto the surface formed by the reaction of cesium with oxidized silver and the evaporation of silver onto a surface formed by reacting cesium with a layer of CsO<sub>2</sub> prepared on a quartz or silver substrate.

The silver oxide cathodes were prepared by the evaporation of a silver surface onto the phototube wall, oxidizing in a glow discharge to the desired extent, evacuating, and reacting the oxide surface with cesium at 150°C to promote the formation of the cesium oxide and to remove excess cesium. The silver evaporator was so constructed that before evaporation of silver onto the surface it could be heated to remove contaminants from the surface of the evaporator. If, as a result of this preliminary heating of the silver evaporator, there was a change in the photosurface characteristics, the phototube was given a stabilizing bake at 130°C before the silver evaporation. The surfaces before the evaporated silver activation exhibited, at most, only a slight photo-response maximum in the range from 500 - 800 mμ and had a thermionic work function of 0.89 ev. The thermionic work function was obtained from the slope of a log i versus 1/T plot. Asao states that the cesium oxide surface contained approximately 5 to 10 excess cesium atoms per 100 Cs<sub>2</sub>O molecules.

The cesium oxide phototube was formed by the deposition on a substrate at  $-180^{\circ}\text{C}$  of a surface cesium layer on and between two evaporated silver contact surfaces deposited on the quartz tube wall. The cesium was then oxidized to  $\text{CsO}_2$  with oxygen, followed apparently by the addition of excess cesium to the oxide at room temperature to convert the  $\text{CsO}_2$  into  $\text{Cs}_2\text{O}$  and thus form a photosensitive surface. The excess cesium introduced during this process was absorbed by colloidal graphite in a side tube. The layer had a thickness of the order of 1000A and appeared to have a very faint yellow color. From the discussion it is not clear whether or not the surface was given a bake at a high temperature to establish phase equilibrium. This surface exhibited a high electrical resistance and the conductivity was characteristic of a semiconductor (decreased resistance with increased temperature). During the conductivity measurements (at 100, 50, 20, and  $-180^{\circ}\text{C}$ ) the conductivity decreased during the course of each measurement. The room temperature resistance of one cesium oxide surface, for example, changed from  $4 \times 10^6$  to  $1.5 \times 10^8$  ohms during the conductivity measurement. It is then clear that these surfaces do not represent an equilibrium state for the distribution of cesium. This surface had (1) no selective maximum between 500 and 800  $\text{m}\mu$ , (2) a long wavelength limit somewhat beyond 1000  $\text{m}\mu$  and (3) a low photosensitivity as compared to the surface formed with silver oxide.

In passing, it is worthwhile to note that these photosurfaces studied by Asao apparently correspond to the surfaces, described later, which were prepared by introducing excess cesium. At  $150^{\circ}\text{C}$  it is very difficult to modify the composition by distillation of excess cesium away from the photosurface to produce a surface with high infrared sensitivity (see Section 3.32).

It is convenient to summarize Asao's results in outline form as follows:

1. The photosensitivity of a thin oxide film photosurface (50 - 100 molecular layers) may be increased several fold by the evaporation of a limited amount of silver on the surface at room temperature or higher ( $100^{\circ}\text{C}$ ). A further increase may be obtained by baking the surface at an elevated temperature.
2. The evaporation of silver onto a thick oxide photosurface does not increase the photoemission except for special processing conditions. The surface obtained under the special, though unstated, conditions exhibits high sensitivity in the range

from 600 - 800  $m\mu$  but much less in the region beyond 850  $m\mu$  than a good infrared-sensitive thick oxide photosurface (long wavelength limit 1100  $m\mu$  compared to 1300  $m\mu$ . See Section 3).

3. The evaporation of silver onto a thin oxide surface at liquid air temperature results in an immediate decrease in sensitivity no matter how small the amount deposited.
4. During the evaporation of silver to obtain maximum photoemission, the thermionic emission decreases exponentially without a change in the thermionic work function (0.89 ev).
5. For a thin oxide layer the maximum sensitivity is obtained when the amount of silver added is equivalent to 2 atoms of added Ag per  $Cs_2O$  molecule present as defined by the original amount of oxygen deposited during silver oxidation.
6. The evaporation of silver results in the formation of a selective maximum in the range 600 - 900  $m\mu$  and the long wavelength limit may increase or decrease depending upon the conditions of the experiment. With sufficient silver, and before maximum photoemission is obtained, there appears to be a definite decrease in the long wavelength limit.
7. The electrical conductivity of the silver-oxygen-cesium cathode is metallic in character and is increased during silver evaporation (resistance changes from 120 ohm/cm<sup>2</sup> to 60 ohm/cm<sup>2</sup>). (The resistance unit refers resistance between two contact strips at opposite edges of a square 1 cm on each edge. Current flow is parallel to the surface.) Metallographic examination demonstrates the presence of rather coarse silver grains in the surface.
8. The deposition of copper on a Cs-Cs<sub>2</sub>O-Cs, Cu(Cu) cathode produces a marked increase in the integral photoemission and the development of a maximum in the 600 - 700  $m\mu$  range.
9. Deposition of copper on the Cs-Cs<sub>2</sub>O-Cs, Ag(Ag) cathode produces an increase in the emission between 500 - 800  $m\mu$  but a decrease at longer wavelengths so that the integral sensitivity remains

essentially constant.

10. The evaporation of silver modifies the transmission and reflection characteristics of the photosurface as a function of wavelength. In particular, the reflecting powder from 500 to 900  $m\mu$  is markedly increased. This is shown in Fig. 2 which is a copy of Fig. 16 in Part I of Asao's report.
11. Evaporation of silver onto a cesium oxide quartz base and a cesium oxide silver base photosurface results in some twenty fold increase in photosensitivity, and the development of a selective maximum in the wavelength range 600 - 750  $m\mu$ . In addition, the observed large photoemission at  $\lambda < 350 m\mu$  is markedly reduced by the addition of silver atoms.
12. For wavelengths greater than 500  $m\mu$  the cesium oxide quartz surface is very transparent, absorption occurring primarily at wavelengths shorter than 500  $m\mu$ . This is illustrated in Fig. 3, a copy of Asao's Fig. 2 in Part II of his report (ref. 23).
13. The evaporation of silver on the cesium oxide quartz surface results, in contrast to the previous cell containing reduced silver, in the production of selective maxima in the reflecting power of the surface in the range 600 - 800  $m\mu$  and a high transmission region near 300  $m\mu$  which is related to the selective transmission maximum of silver at these wavelengths. These data are also illustrated in Fig. 3.
14. On cooling both types of cathodes (quartz and silver oxide silver base) to liquid air temperatures, a marked increase in the photoemission occurred over the entire wavelength range from 500 to 1200  $m\mu$ .

From the experimental data Asao draws several interesting conclusions relating to the role of silver in increasing the photoemission. He considers a model for the cathode consisting of an intermediate layer of cesium oxide containing adsorbed (internal and surface) cesium atoms and reduced (i.e., resulting from the reaction between cesium and silver oxide) silver atoms.

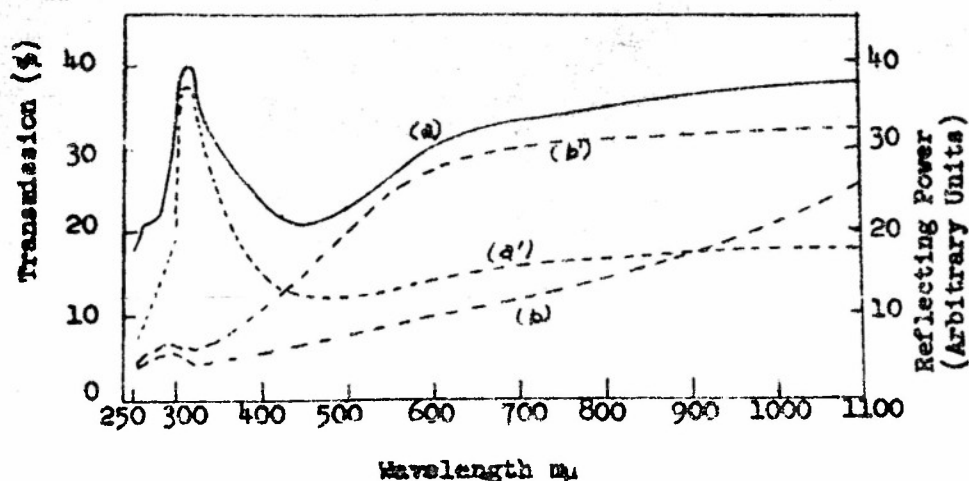


FIG. 2. SPECTRAL TRANSMISSION OF Cs-Cs<sub>2</sub>O, Cs, Ag (QUARTZ) BEFORE (a) AND AFTER (a') CONDENSATION OF SILVER ATOMS. SPECTRAL REFLECTIVITY FOR Cs-Cs<sub>2</sub>O, Cs, Ag (QUARTZ) BEFORE (b) AND AFTER (b') CONDENSATION OF SILVER ATOMS (ASAO'S FIG. 16, PART I OF REF. 23).

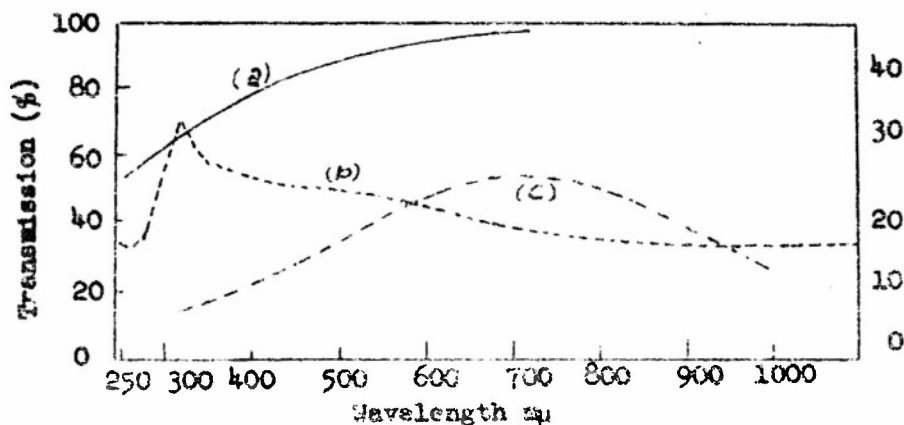


FIG. 3. SPECTRAL TRANSMISSION AND REFLECTIVITY OF THE FILM Cs-Cs<sub>2</sub>O, Cs (QUARTZ) BEFORE AND AFTER DEPOSITION OF SILVER ATOMS. (ASAO'S FIG. 2, PART II OF REF. 23).

- (a) SPECTRAL TRANSMISSION OF FILM Cs-Cs<sub>2</sub>O, Cs (QUARTZ)
- (b) SPECTRAL TRANSMISSION OF THE FILM Cs-Cs<sub>2</sub>O, Cs (QUARTZ) WITH CONDENSED SILVER ATOMS
- (c) SPECTRAL REFLECTIVITY OF Cs-Cs<sub>2</sub>O, Cs (QUARTZ) WITH CONDENSED SILVER ATOMS



The reduced silver atoms are assumed to be present in the ratio of 2 Ag/Cs<sub>2</sub>O molecule. (This proportion is not accurate since the glow discharge oxide phase is not solely Ag<sub>2</sub>O. See Part I of this final report series). However, Asao considers that the reduced silver is distributed as (1) colloidal silver grains and (2) atoms in the cesium oxide, i.e. a solid solution or compound. Electrical conductivity in the silver oxide cathode is assumed to result from overlapping of silver grains.

The silver atoms deposited during the activation are assumed to (1) aggregate with the reduced silver particles and (2) diffuse into the intermediate Cs<sub>2</sub>O layer. This latter deduction is based upon the observation that evaporation of a thin film of silver on the Cs<sub>2</sub>O-quartz surface does not change the conduction to metallic conduction (i.e., the surface remains a semiconductor) and that evaporation of a 2 - 3 atom layer of silver onto the surfaces maintained at -180°C results in a decrease in sensitivity but warming to room temperature results in an increase. The evaporation onto a surface at -180°C presumably prevents diffusion into the interior, but such diffusion occurs in the subsequent warming and is accompanied by increased photosensitivity. These observations are certainly compatible with the idea that diffusion of silver into Cs<sub>2</sub>O contributes to the increased photosensitivity. In view, however, of the marked tendency of thin silver films to aggregate into clusters of isolated grains, with the resulting film having high resistance, we wonder whether grain contact would be established in these experiments even if no diffusion took place. This question is certainly pertinent in view of the recent work of Sennett and Scott<sup>28</sup> which so clearly shows the isolation of silver grains in thin films on a formvar substrate. In spite of this unanswered question these observations of Asao are of great interest and are, as stated earlier, compatible with the diffusion hypothesis.

The work of Asao shows conclusively that added silver has an important influence on photoelectric yield. Asao proposed that the added silver, in some unexplained way, increased the probability of ejection of photoelectrons from adjacent cesium atoms. Sayama<sup>31</sup> has considered another, and more obvious, explanation, i.e., that the finely dispersed silver in the photocathode constitutes the source of photoelectrons. Sayama's work is more fully reviewed in Section 1.6. It has been found that the evaporation of other metals than silver onto a photocathode also increased the photosensitivity (see ref. 22). The

effect is not, therefore, specific. We shall return again to the discussion of the effect of silver in the photocathode in Section 1.6. It is clear from the preceding summary that Asao's work also contributes something to the understanding of the role of Cs<sub>2</sub>O in the photocathode. This is further discussed in Section 1.5 and again, briefly, in Section 1.6.

#### 1.43 Effect of silver base on photocathode

It has already been pointed out in Part I of the present report series that the silver base has an important influence on infrared sensitivity of a photocathode. The evaluation of this factor is an old problem because of the industrial importance of two types of photocathodes, one prepared on a massive silver base and the other on a semitransparent silver film. Some practical devices employed to improve sensitivity of the latter cathode have already been mentioned in Section 1.2, and the work of Asao provides a very detailed systematic study of the effect of additional silver on photocathode properties. A systematic study of the effect of the silver base has recently been made by Morozov and Butslov<sup>4</sup> and it seems worthwhile to briefly describe the results.

In order to study the influence of silver film thickness on photoelectric response, tubes were prepared on an evaporated silver base of varying thickness. After oxidation and cesium addition the spectral yield was determined at each of several positions of different thicknesses. Transmission as a function of thickness was also determined on the original silver film. (In actual fact the variable parameter used to characterize the film is the number of micrograms ( $\mu\text{g}$ ) per square centimeter rather than thickness.) Five spectral yield curves are given covering the range from 7 to 14  $\mu\text{g}/\text{cm}^2$ . If the void volume were zero this would correspond to a thickness range from 70 to 140 Å. In passing from the thin to the thick section the spectral yield undergoes a marked change in which infrared sensitivity increases considerably. At 7  $\mu\text{g}/\text{cm}^2$  the spectral yield has a slight maximum at about 450 m $\mu$  wavelength while at 14  $\mu\text{g}/\text{cm}^2$  the maximum is at 750 m $\mu$ . These data refer to experiments in which the photocathode is illuminated on the same side as that from which electron ejection takes place. At greater thicknesses than that corresponding to 11  $\mu\text{g}/\text{cm}^2$  no further change in spectral response was found.

From the data on percent transmission and electrical conductivity of silver films, given by Morozov and Butslov, it appears that the region of thicknesses from 7 to  $14 \mu\text{g}/\text{cm}^2$  is that in which "grain merging" is taking place, i.e., the region marking the transition from a condition in which very small silver grains rest on the substrate in isolation from each other to that condition in which the grains merge to form a continuous film with little, if any, void volume. (This transition has been beautifully illustrated in the recent work of Sennett and Scott<sup>15</sup>). This is confirmed by the fact, as pointed out by Morozov and Butslov, that the film resistance drops from  $10^{12}$  to  $10^3$  ohms/cm<sup>2</sup> on passing through the transition region. Although the evaporation time was not given, it appears from comparison of the transmission data with that of Sennett and Scott<sup>16</sup> that a "fast" evaporation is indicated ( $\sim 2$  sec).

In the light of our own work on the effect of silver film thickness it seems worthwhile to interpose a few remarks at this point concerning the above work. It is not particularly surprising that a marked change in spectral response should accompany the "grain merging" process described above merely on the basis of establishing electrical contact between various sections of the photocathode, although it is good to have the specific nature of the change clearly illustrated. Morozov and Butslov found, however, that further increase in the film thickness did not alter the spectral response. Results obtained in the present work show that this is not always the case. In a series of photocathodes prepared on a base consisting of an evaporated silver film 10,000 Å thick a pronounced effect of silver base was found. Either by increasing the thickness to 30,000 Å or by reducing the evaporation rate, a marked increase in infrared sensitivity could be brought about. It is of interest to note that the spectral response obtained with 10,000 Å films, evaporated rapidly, were in many cases rather similar to those obtained by Morozov and Butslov on films containing  $14 \mu\text{g}/\text{cm}^2$  of silver. Spectral responses obtained on increasing the thickness to 30,000 Å had maxima at about 900 m $\mu$  and the cathodes were in general much more sensitive in the infrared. In brief, the structure of the silver base may affect spectral response up to thicknesses as great as 10,000 Å, much beyond the thickness at which silver "grain merging" takes place. If, however, the silver base has been properly prepared, the increase in infrared sensitivity can be brought about at thicknesses less than 10,000 Å, although the lower limit has not been determined. These remarks do not imply that the work of Morozov and Butslov is in error; in fact, we have performed

experiments similar to theirs with perhaps less care and obtained similar results, but it is evidently true that two different effects can occur, one related to grain merging which sets in at around 100Å and another, whose cause is unknown, which operates at much greater thicknesses. The latter is erratic in the sense that it depends sensitively on film preparation. Our results are discussed in Sections 3.51 and 4.12 of this report. A brief summary has been given in Part I of the present report series. In that report (Part I) it is also shown that the chemical products of silver oxidation change abruptly in passing through the region in which grain merging takes place. This corresponds to the region from 7 to 14  $\mu\text{g}/\text{cm}^2$  in Morozov and Butslov's experiments.

Morozov and Butslov also studied the effect of the extent of oxidation on photoelectric yield. Cathodes prepared by oxidation to a blue color had higher infrared sensitivity than those less oxidized. The maximum in spectral response shifted to shorter wavelength with decreased extent of oxidation. Others have also observed this although the data are less extensively reported (see e.g. Ives and Olpin, ref. 29; also ref. 30). During the course of the present research an example has also been encountered in which markedly different spectral responses were encountered in tubes oxidized to different degrees. (See Section 3.16 for an example.)

In describing their results Morozov and Butslov gave no detail concerning the method of preparation, and hence we are unable to compare closely their results with our own at least not beyond the above general comments.

From the discussion of Sections 1.41 and 1.42 it is evident that the silver base may affect photocathode properties because the addition of cesium to oxidized silver results in the displacement of silver from the oxide. The resulting metal collects in part as fairly large metal grains and in part as very finely dispersed metal scattered through the photocathode. In Part I of this report series evidence is brought forward that the oxide produced on oxidation of silver in a glow discharge, is not merely  $\text{Ag}_2\text{O}$ , but is a complex mixture of  $\text{Ag}_2\text{O}$  with other silver oxides containing more oxygen (perhaps  $\text{Ag}_2\text{O}_3$ ). The proportion of  $\text{Ag}_2\text{O}$  compared to higher oxides is markedly dependent on silver base thickness and, in addition, the proportions may even vary in the incomplete oxidation of massive silver

samples (see Section 4 of this report). This constitutes a potential variable which may affect photosensitivity. For if the oxide were purely  $\text{Ag}_2\text{O}$ , then on reduction with cesium two silver atoms are produced for each oxygen, while if the oxide were entirely  $\text{Ag}_2\text{O}_3$ , then only two-thirds of a silver atom is released for each oxygen atom. For a fixed extent of oxidation, therefore, the amount of finely dispersed silver which is released within the photocathode will depend on the compound of silver formed in oxidation and the compound formed is known to depend on the condition of the base. This constitutes only the most obvious manner in which the cathode can be affected, indirectly, by the silver base. The subsequent effect of different silver oxides on the reaction with cesium remains entirely unknown.

Other base metals than silver have been studied. In an investigation by Kluge<sup>25</sup> the spectral sensitivities were reported for photocathodes fabricated using copper and gold, as well as other metals, as the base. The cathode fabricated on a silver base has, however, much the highest infrared sensitivity. The fact that the long wavelength maximum is markedly dependent on the base metal used shows that this maximum is not due entirely to  $\text{Cs}_2\text{O}$  and adsorbed cesium atoms. The pronounced effect of base metal shows that it is also involved, probably in the form of finely divided metal released on adding cesium to the base metal oxide and scattered through the  $\text{Cs}_2\text{O}$  layer.

It was also found by Kluge that the substitution of a roughened silver base for a specular reflecting silver base considerably increased infrared sensitivity<sup>26</sup>. In an example given by Kluge the long wavelength maximum shifted from 750 to 875  $\text{m}\mu$  on substituting a rough silver base for a specular base. This may be connected with uniformity of oxidation (see Part I of this series) although Kluge interpreted it as due to an increase in the number of active centers available for adsorption of cesium atoms, in line with de Boer's theory. On this view the increase arises, of course, from the increased surface area for adsorption brought about by roughening the surface. Since such a process may well change the chemical products of oxidation we doubt that the situation is as simple as this.

### 1.5 Role of Cesium Oxide in the Photocathode

From the results of Section 1.4 it is evident that finely dispersed silver scattered through the photocathode



has an important influence on photosensitivity. This is attributed by de Boer, to the increased electrical conductivity of the  $\text{Cs}_2\text{O}$  matrix containing embedded metal particles and perhaps metal atoms dissolved in  $\text{Cs}_2\text{O}$ . There remains now the question as to the function of  $\text{Cs}_2\text{O}$  in the photocathode. Some pertinent observations on this point are discussed in the present section.

It has already been pointed out that Asao studied the transmission and reflection coefficients for thin  $\text{Cs}_2\text{O}$  films on quartz (see Fig. 3). The observations show that these thin films are quite transparent at long wavelengths. Asao concludes, therefore, that the selective maximum in photoelectric yield, for Ag-O-Cs photocathodes, does not arise as the result of a selective adsorption in  $\text{Cs}_2\text{O}$ . This matter has been further studied in more recent work described below. It is incidentally of interest that the  $\text{Cs}_2\text{O}$  films prepared by Asao had a faint yellow color.

In a recent experiment Borziak<sup>1</sup> has reinvestigated the transmission of cesium-oxygen films. In this work a cesium film of graded thickness was evaporated onto a glass base at liquid air temperature using a molecular beam technique. Cesium was then completely oxidized to  $\text{CsO}_2$ , forming a transparent, colorless film. (The substance formed was identified as  $\text{CsO}_2$  by means of a separate experiment in which the combining weights of cesium and oxygen were determined using a sensitive spiral spring balance). When the transparent film of  $\text{CsO}_2$  was treated with cesium at 150 - 160°C an external photoelectric effect developed while the film was still colorless. As the cesium addition was continued the film ultimately became yellow and the photosensitivity (external photoelectrons) became greater. Borziak remarks that the color of  $\text{Cs}_2\text{O}$  is reported as red on the basis of chemical investigation. Moreover, he was able to obtain a red crystalline material by treating the  $\text{CsO}_2$  film with cesium at temperatures above 200°C. The red material so obtained had, however, a much lower photosensitivity than did the yellow film. Borziak concluded that the photosensitivity of cesium-oxygen photocathodes (without silver) is either not due to  $\text{Cs}_2\text{O}$  or the reported color of  $\text{Cs}_2\text{O}$  is wrong. Borziak did not establish by analysis that the yellow compound, described above, had the composition of the compound  $\text{Cs}_2\text{O}$ . Nevertheless, from the description given of the method of preparation, we believe that  $\text{Cs}_2\text{O}$  would result.

Borziak also studied the transmission of the yellow ( $\text{Cs}_2\text{O}$ ) film described above. Only relative transmissions were reported so the results cannot be quantitatively

compared with the work of Asao, although the shape of the transmission curve closely resembles that of Asao. Photo-current as a function of wavelength was also determined at the same point as the transmission. A maximum in photoelectric yield was found at 580  $m\mu$  wavelength, but no selective maximum in absorption was indicated at the same wavelength in the transmission measurements. The results indicate, in agreement with Asao, no selective maximum in absorption which could account for the selective maximum in photoelectric current. The photoelectric yield as a function of wavelength obtained by Borziak for  $Cs_2O$  is not in very good agreement with that of Asao since the latter found either no selective maximum or a very small one. Since photoelectric yield is very sensitive to the method of preparation this is perhaps not surprising.

There is one remaining point of some interest. The absence of an absorption band in  $Cs_2O$  is somewhat surprising. We have repeatedly found that  $Cs_2O$  is colored (see Section 1.1). The typical pale orange color has been reported by others and is observed not only in polycrystalline samples but also in the microscopic examination of single crystals. The color varies with temperature (see Section 1.1) from a faint yellow at liquid air temperature to red at  $200^\circ C$ . The source of color is unknown. The crystal structure of  $Cs_2O$  is unusual for oxides of type  $M_2O$  but a crystal structure determination (see Part III of this series) has confirmed the layer type anti- $CdCl_2$  arrangement. Moreover, lattice energy calculations based on the assumption that the crystal contains  $Cs^+$  and  $O^{2-}$  ions leads to rather close agreement with the observed lattice energy provided the high polarizability of  $Cs^+$  is taken into account. The crystal seems, in brief, to be a normal ionic crystal which has the unusual (for alkali oxides) layer structure because of the high polarizability of  $Cs^+$ . On empirical grounds we do not expect a color for such a substance since solutions containing  $Cs^+$  are not colored. We believe it to be possible, even probable, that impurities are responsible for the color, although a clearcut proof is not available. If this is true then a nonstoichiometric compound might be indicated. However, analysis for excess cesium in one typically colored sample indicated an excess of only one-tenth atomic percent. Although this might be sufficient to account for the color it would nevertheless be of considerable interest either to prove or disprove it. The point is emphasized here because the color of  $Cs_2O$  is temperature dependent and so is the photoelectric yield from a  $Ag-O-Cs$  photocathode. Until this point is cleared up, the possibility will remain that the color of  $Cs_2O$  may be connected with the mechanism of the



photoelectric effect. The parallel with F-centers in the alkali halides is certainly suggestive.

As stated above, the work of Asao and that of Borziak do not reveal any selective maximum in adsorption which could account for the selective maximum in photoelectric yield in the Ag-O-Cs photocathode. This observation is brought into more accurate perspective when we consider the quantum yield of photoelectrons from a photocathode. It has been found that less than one percent of absorbed light is effective in producing photoelectrons<sup>49</sup>. This applies to light in the wavelength region 500 to 1000 mμ. It is quite clear that the determinations of percentage transmission are not accurate enough to detect an absorption band contributing less than one percent to a general absorption which does not produce external photoelectrons. This was clearly recognized by Borziak.

The role of Cs<sub>2</sub>O in the photocathode is far from clear. Whether the substance has a specific function in the cathode has not been established. In one theory of the photocathode it is ignored entirely (see Section 1.6), whereas in the theory of de Boer it merely provides a medium for the strong adsorption of cesium atoms. Despite the experimental work mentioned in Section 1.3, Borziak has raised the question of whether Cs<sub>2</sub>O is a cathode constituent and at one stage of our own investigation the same question arose in our minds. We have, however, conclusively identified the substance in infrared-sensitive photocathodes (see Section 4) and it constitutes the predominant constituent. It seems probable, however, that impurities are essential in order that photoelectrons should be produced. Further comment on the role of Cs<sub>2</sub>O in the photocathode is made in Section 1.6. The matter is considered again in Section 5.

The work of Kluge<sup>27</sup> illustrates very well the differences between photoelectric yield obtained when other alkali metals (Na, K, Rb) are substituted for cesium. The cathodes prepared using cesium had long wave maxima furthest in the infrared. Incidentally, Kluge<sup>27a</sup> found that the long wave maxima disappeared when small amounts of oxygen were admitted to the photocathode. These experiments have been further discussed by de Boer<sup>22</sup>. The latter experiments have been widely interpreted as supporting de Boer's theory which attributes the long wave maxima to adsorbed cesium atoms.

## 1.6 Optical Properties of Photocathodes

In order to fully convey the significance of the optical investigations which have been made on photocathodes it seems necessary to discuss briefly the salient factors which contribute to photoelectric yield. For the purposes of this discussion it is useful to consider the contribution to photoelectric current, produced in a small volume element of the photocathode, as proportional to the product of four factors: (1) the energy density of the electromagnetic field averaged over one cycle, (2) the probability of electronic excitation (per unit energy density) by radiation absorption, (3) the probability that a photoelectron produced in step 2 will reach the vacuum-cathode interface with enough energy to escape, and (4) the probability that the photoelectron of step 3 on approaching the barrier at the interface will escape into the vacuum. The electronic excitation probability of step 2 above is presumed to be that for the production of a potential external photoelectron, i.e., one which has the proper energy etc. so that it could escape into the vacuum if the factors (3) and (4) are favorable. The theoretical expression of photoelectric current as a product of factors is no doubt too simple to be rigorously valid for the overall process. To be more accurate the excitation probability should be to a state with momentum components in a specified range and similarly for the other steps. The total photocurrent would then be obtained as a multiple integral over all momentum components. In this case each elementary process contributes to the photocurrent to a degree expressible as a product of factors and the total current is the sum of all such elementary contributions. For the qualitative purposes which we have in mind the total current can be considered proportional to the product of four terms, each being an appropriate average over all possibilities.

Before passing on to a discussion of experimental results we note first the distinction between surface and volume photoelectric effects. If the second factor above, excitation probability, has a significant value only in the immediate vicinity (a few atomic layers) of the cathode-vacuum interface then a surface photoelectric effect prevails. If, on the other hand, the excitation probability has a substantial nonvanishing value throughout the internal volume of the photocathode, then we are dealing with a volume photoelectric effect. It must be emphasized that even in the case of a volume photoelectric effect the actual photosensitive volume which contributes to the production of

external photoelectrons may be a thin layer near the surface. For the third factor above may limit the effective range which an electron may traverse and still escape.

With these explanations out of the way we now proceed to a discussion of the experimental work. All of the effect of light interference is concentrated in the first factor above, i.e. the electromagnetic field energy density. This factor (the optical factor) is also sensitive to the angle of incidence of the incident light and to its state of polarization. This fact has been used with great effectiveness by H.E. Ives and collaborators in the study of composite photocathodes. The photocathodes studied most extensively were those in which a thin layer of an alkali metal was deposited on a base metal (silver or platinum). As the result of this study it is established that photoelectrons come, in all cases, from a thin layer near the cathode vacuum interface. By "thin" is meant a layer whose thickness is small in comparison to the wavelength of light. The layer might well have a thickness much larger than a molecular layer and still be small compared to the wavelength of light. Specific instances are given in a paper by Ives and Briggs<sup>26</sup>. References to earlier work, in which important results are obtained, are also given in this paper. For our purposes the method used is the important consideration. The field energy changes with angle in a highly characteristic way which tends usually to overshadow the slow change of the remaining factors. If, therefore, the photocurrent is measured as a function of angle and compared with the energy density at the surface computed from known optical constants, then at a given wavelength, a very clear parallel between the dependence of these two quantities (photocurrent and energy density) can frequently be found. For example, the hypothesis of a thin photosensitive layer was established by comparing the trend with angle of energy density and photocurrent for a composite cathode using light polarized parallel to the plane of incidence in one series of experiments and perpendicular to the plane of incidence in another. In order to obtain energy densities which parallel photocurrent with approximately the correct ratio (for parallel and perpendicular polarization) it is necessary to compute the energy density just above the base metal (and hence within the alkali metal film). Very poor agreement is obtained when the total energy density, throughout the depth of light penetration, is computed. The success achieved by this attack has led to its

application to Ag-O-Cs photocathodes.

It was proposed by de Boer and Teves (see ref. 22) that the source of photoelectrons in the Ag-O-Cs cathode is cesium atoms adsorbed on the surface of Cs<sub>2</sub>O. This suggests, as an approximation, that the system be considered as consisting of a thin layer of sensitive material separated from the base metal by a dielectric layer. Ives and Olpin<sup>29</sup> performed experiments designed to test this model. Calculations were first made of the energy density just above the dielectric layer since this was the presumed position of the photosensitive layer. Energy density was computed, at each of several wavelengths, as a function of angle and thickness of dielectric layer for light polarized, respectively, parallel and perpendicular to the plane of incidence. Calculations were performed using optical constants for quartz (the dielectric layer) and those of silver and platinum respectively for the metal base. The interference patterns obtained in this way are very complicated. There is, in addition, a marked difference between the patterns calculated for a thick dielectric layer and those computed for a layer of zero thickness. It seemed reasonable to suppose, therefore, that the characteristic changes in interference pattern with angle of incidence could be recognized in the experimentally determined photocurrents.

Experiments were then performed, by Ives and Olpin, on photocathodes in which photoelectric yield was measured as a function of angle of incidence for both perpendicular and parallel polarized light at a number of wavelengths. If the thickness of dielectric layer is properly selected then the variation in energy density, calculated for quartz on platinum, does indeed show a trend with angle (at constant wavelength) which is very closely similar to that found by experiment for the photocurrent. The calculated curves of energy density vs. angle for parallel and perpendicular polarized light cross each other in a highly complicated way and the same behavior is also observed for the photocurrents. Moreover, the whole character of the angular trend undergoes a change when the thickness of the layer is reduced. Photocathodes having thin layers were also prepared by reducing the extent of silver oxidation and again the trend in photocurrent paralleled the calculated trend of energy density. The agreement is impressive. On the other hand, this close parallel is not found between photocurrent and energy density when wavelength, rather than angle, is the variable. Hence the spectral response is not determined by interference of light, although this factor no doubt has an influence. Instead, the electronic

excitation probability, factor 2 of the first paragraph, is apparently strongly dependent on wavelength. In particular, the maximum in spectral response is not due to an interference phenomenon but to factor 2 (and 4) discussed above. Although the optical constants used by Ives and Olpin are now known to be far from accurate, nevertheless this conclusion seems to be verified in subsequent work.

In all of the calculations the photocathodes used were assumed to be specular reflectors. In order to achieve this the photocathodes were prepared on specular silver bases. The cathodes were tested, by observing interference fringes both after oxidation and after cesium addition, in order to verify that at least an approximation to specular reflection was obtained.

Ives and Olpin conclude that their experiments provide clear evidence that photoelectrons originate in a thin layer raised above the metal base and separated from it by a thin layer, presumably dielectric. They also point out that the thin active layer is not necessarily a monolayer. It is only necessary that thickness be smaller than the wavelength of light. It was in fact, pointed out that a considerable thickness of  $\text{Cs}_2\text{O}$  layer is necessary in order to obtain a high photoelectric yield. This fact seems to point toward a layer of substantial thickness. The "dielectric" layer is, in fact,  $\text{Cs}_2\text{O}$  containing colloidal metal particles, and perhaps other impurities, and the photosensitive layer may be a slice of this same "dielectric" situated adjacent to the cathode-vacuum interface. None of this has, however, any effect on the Ives and Olpin hypothesis that the electromagnetic field which is effective in producing photoelectrons is the field in a thin layer near the cathode surface. In fact, subsequent work supports this hypothesis. The assumption of a nonabsorbing dielectric layer is not, however, supported by subsequent work.

The most obvious weakness of the Ives and Olpin theory lies in the very rough approximations to optical constants. Their work serves chiefly to show that by properly selecting optical constants the observed trends with angle can be accounted for. They did not show, however, that those constants conform to the optical constants of the actual cathode material. This matter has been further studied in recent work which is considered later.

An interesting and definitive research, using polarized light, has been reported by Kluge<sup>30</sup>. In this work, photo-



cathodes were prepared on bases consisting of specular reflecting silver mirrors prepared by evaporating silver on glass. Results are reported for two silver-oxygen-cesium photocathodes, one containing a Cs<sub>2</sub>O layer 50 m $\mu$  thick and another 20 m $\mu$  thick. The spectral yield curve for the former has a maximum at 800 m $\mu$  (high infrared sensitivity) while the latter has no maximum at this wavelength (low infrared sensitivity). The photocathodes were tested for specular reflection by replacing the light detector by a photographic plate and comparing the image of the monochromator exit slit with the image obtained in the same way but with the cathode replaced by an unoxidized silver mirror. The results clearly show that diffusely scattered light is negligible (see Figs. 4a and 4b of Kluge's paper), since the slit images are as clear and sharp on reflection from a cathode as from a silver mirror. With an angle of incidence of 55°, for light on the photocathode, spectral yield curves are obtained in three cases, (a) unpolarized light, (b) light polarized with electric vector parallel to the plane of incidence, and (c) light polarized with electric vector perpendicular to the plane of incidence. For the 50 m $\mu$  thick photocathodes the selective maximum at 800 m $\mu$  was obtained in all three cases while for the thin (20 m $\mu$ ) cathode the selective maximum was absent in all three cases. Moreover, since the cathodes were specular reflectors, measurement of the intensity of reflected light provides a direct measurement of light absorbed by the photocathode. The percentage of incident light which is reflected is given under each of the above experimental conditions. For the thick (50 m $\mu$ ) cathode 95% of the incident light is absorbed at 600 m $\mu$  wavelength and 80% is absorbed at 800 m $\mu$ . At 1200 m $\mu$  only 10% is absorbed. In the same wavelength range (500 - 1200 m $\mu$ ) a silver mirror absorbs only about 5% of the incident light. These figures apply to unpolarized light. It is found for the thick cathode (50 m $\mu$ ), which exhibits a typical selective maximum at 800 m $\mu$ , that the light absorption does not parallel the photocurrent. This applies whether the light is polarized or unpolarized. Moreover, the spectral yield at the selective maximum (800 m $\mu$ ) is approximately  $2.2 \times 10^{-3}$  coulombs/calorie of incident radiation (unpolarized). Hence  $0.81 \times 10^{-3}$  external photoelectrons are produced per quantum (800 m $\mu$ ) of incident light and, since 80% of the light is absorbed,  $1 \times 10^{-3}$  electrons are produced per quantum absorbed. This establishes that one quantum per thousand absorbed is effective in ejecting a photoelectron from the photocathode. In view of this fact it is hardly surprising that no selective maximum in absorption can be found which parallels the maximum in photocurrent. For a photoelectrically active

absorption superimposed on a general absorption a thousand times greater would not be detected in these experiments.

In order to orient ourselves it is useful to compare the layer thickness of Kluge's cathodes with layer thicknesses for typical cathodes. A massive cathode, prepared by oxidizing silver to the second order yellow color, contains  $4.6 \times 10^{-7}$  gram atoms oxygen per square centimeter. A typical semitransparent photocathode contains  $1 \times 10^{-7}$  gram atoms of oxygen per square centimeter. Assuming that all oxygen ultimately ends in  $\text{Cs}_2\text{O}$  and using the volume per molecule for  $\text{Cs}_2\text{O}$  (98.7 cubic Angstroms) we find for the thicknesses 270  $\text{m}\mu$  and 59  $\text{m}\mu$  respectively in the above two cases. The thick cathode used by Kluge has a  $\text{Cs}_2\text{O}$  layer whose thickness is comparable with that for a semitransparent cathode. Kluge's cathode was, of course, not semitransparent because a thick silver base was used. The thin cathode is much thinner than that normally used in a semitransparent commercial cathode. His success in obtaining specular reflecting cathodes was due, as he stated, to the fact that a thin  $\text{Cs}_2\text{O}$  layer was used. The thickness being about one-tenth the wavelength of light, large particles could not develop and hence scattering is at a minimum. Specular reflection occurs because the base is specular. At the same time the cathodes do not have maximum infrared sensitivity. For Kluge<sup>26</sup> has reported that replacement of the specular base by a roughened base leads to a long wave maximum at longer wavelengths, and to higher sensitivity.

One fact arising from Kluge's work is of some interest. It is obvious that the cathode absorbs strongly. Hence the Ives and Olpin assumption of optical constants for quartz is inaccurate since quartz does not absorb strongly in the infrared. The thin (20  $\text{m}\mu$ ) cathode absorbed 40% of the incident radiation at 800  $\text{m}\mu$  wavelength. It is obvious from these figures that a thick film such as that encountered in massive cathodes will absorb the incident radiation almost completely before it penetrates to the base metal<sup>27</sup>.

Kluge found that parallel polarized light gives higher photoelectric yield than does perpendicular polarized light at wavelengths greater than 500  $\text{m}\mu$  for both the thin and thick cathodes. The ratio is roughly two to one. In addition, the results of two runs are given in which the angle of incidence is varied. Here again the photoelectric yields are in the same order and



the ratio has a maximum of about 2 to 1 at  $55^\circ$ . These results have been interpreted by de Boer (ref. 22) as favoring his theory which attributes the production of photoelectrons to photoionization of adsorbed cesium atoms. This apparently assumes, however, that ionization probability is strongly dependent on the direction of the electric vector. It seems much more likely, however, that the differences between photoelectric yield observed by Kluge, using parallel and perpendicular polarized light, are due largely to the fact that energy densities for parallel and perpendicular polarized light are different at 50  $\mu$  above the base metal because of interference. This agrees well with figures given in Ives and Olpin's paper and with earlier calculations by Ives of the energy densities just above a metal surface. Ives and Olpin point out that a photoelectric absorption seems indicated which is not strongly dependent on the plane of polarization of incident light (factor 2 of the first paragraph of this Section). This seems quite reasonable and, in our opinion, can be more readily understood if a volume photoelectric effect is involved.

From the above work of Kluge it is evident that only a small fraction of the absorbed radiation is effective in producing photoelectrons. We now pass on to the consideration of some theoretical and experimental work in which attempts are made to locate the absorption which is responsible for photoelectron production.

Sayama<sup>31</sup> has developed a theory of photoelectric emission which is essentially an extension of that of Ives. The theory is, however, developed for a semitransparent rather than a massive cathode and the cathode is assumed to be homogeneous. This theory is based on Asao's observation that the reflection and transmission coefficients for a  $\text{Cs}_2\text{O}$  film with added, evaporated, silver are very similar to those for a pure silver film of comparable thickness. Sayama has therefore performed calculations in which the optical constants of the photocathode are replaced by those of thin silver films, i.e., the contribution of  $\text{Cs}_2\text{O}$  is neglected entirely. The work function is assumed to be lowered, in some manner, to that observed for the actual photocathode. A volume photoelectric effect is assumed with the photoelectrons originating in silver. The photoelectric yield is then proportional to the radiation absorption per unit field energy multiplied by the energy density of the electromagnetic field in a layer, near the surface, thin enough for the electrons to escape. Computations were made of photoelectric yield vs. wavelength for several sets of optical constants appropriate to various

silver film thicknesses. If the optical constants of bulk silver are used then the calculated yield has no maximum at any wavelength. If, however, the optical constants for a thin film are used, then a selective maximum is found. The maximum does not come at quite the proper wavelength, but in view of the very rough approximations involved this is hardly surprising. The whole theory is rough but it does illustrate one important point. The selective maximum in photoelectric yield is again not due to the very complicated interference of light, which appears in the energy density term, but is due to radiation absorption by the silver particles.

It is a well known fact, that selective absorption occurs in thin silver films because the film consists of small particles. This is conclusively shown by the work of Sennett and Scott<sup>28</sup> who measured the absorption coefficients for silver films and, at the same time, determined the particle sizes in the films by means of an electron microscopic investigation. This work shows that absorption is a maximum at sizes just below that at which grain contact is established. Taking this into account we can then interpret Sayama's theory in slightly more realistic terms. The theory proposes essentially that photoelectrons are produced in colloidal silver particles embedded in a layer of  $\text{Cs}_2\text{O}$ . It must be emphasized that the present paragraph constitutes our own interpretation of the significance of Sayama's theory and is not a quotation from the author.

It was pointed out earlier, in discussing Asao's work, that  $\text{Cs}_2\text{O}$  films are transparent in the infrared, and hence Asao concluded that selective absorption in  $\text{Cs}_2\text{O}$  was not responsible for the selective maximum in photoelectric yield. Excess silver, according to Asao, is essential. The theory of Sayama puts these ideas into semiquantitative form. The theory has obvious weaknesses, but also undeniable merit. In the first place it focusses attention on the fact that impurities play an important role. We are not dealing with pure, perfectly ordered  $\text{Cs}_2\text{O}$  crystals. Second, it suggests that other metals finely dispersed in  $\text{Cs}_2\text{O}$  may also play a role, as is observed to be the case (see ref. 22). The biggest weaknesses are: (a) the reason why  $\text{Cs}_2\text{O}$  is essential is not indicated, (b) the assumptions concerning optical constants are too approximate, and (c) the reasons for a low work function are not given.

We note finally that Sayama assumes a volume photoelectric effect. Sayama gave no justification for this hypothesis. We have already pointed out, however, that the

observations of Ives and Olpin seem to us to support this view although, of course, the interpretation is only qualitative.

Some interesting experiments, which bear on the above work, have recently been done by Borziak and Margulis<sup>2</sup> and by Borziak<sup>1</sup>. These investigators have attempted to determine the refraction and absorption indices, for semitransparent cathodes, as functions of the wavelength. Moreover, the photoelectric emission has been correlated with reflection and transmission coefficients of thin films by means of direct observation.

Borziak and Margulis studied interference patterns in a thin wedge-shaped photocathode. The cathode was prepared by evaporating a thin silver film of graded thickness onto a glass substrate bounded by two parallel platinum contact strips which were also covered by the evaporated film. The substrate was maintained at liquid air temperature. This film was then made the cathode in a slow discharge through oxygen. As the film warmed up the oxidation proceeded slowly until a colorless film showing a clear interference pattern was obtained. The reflection coefficient for the oxidized film was then determined. Cesium was then added to produce a photocathode. The reflection coefficient as a function of position along the wedge and the photoelectric current were simultaneously determined using monochromatic light. Direct illumination was used in the first experiment (i.e. illumination from the vacuum side of the cathode). In the thick sections of the film the direct photocurrent is found to be a periodic function of the thickness and is opposite in phase to the reflection coefficient. This means, according to Borziak and Margulis, that the electromagnetic field near the electron emitting surface is that responsible for production of photoelectric current. This agrees with the conclusion of Ives and Olpin. In the thin sections of the films a sharp maximum in photocurrent is finally reached and beyond, i.e. toward thinner sections, the photocurrent falls rapidly to zero. Borziak and Margulis point out that the maximum occurs at the point where the thickness of the active layer, i.e., the layer from which photoelectrons can escape, becomes comparable with the film thickness. This interpretation is confirmed by further investigation of the reverse photocurrent and the transmission of the film. It is important to note that the sharp maximum in the thin film sections is not an interference maximum beyond which the energy density of the electromagnetic field goes down. The situation is the

reverse. The field energy rises steadily as the thickness decreases, hence the only explanation is that the volume of the active layer is decreasing. This assumes, of course, that the wedge is homogeneous, a questionable point.

The thicknesses (dm) at the maximum, which are rough measures of the thickness of the active layer, are given at various wavelengths in the following table.

$\lambda, m\mu$	$dm, m\mu$
420	45
500	47
600	55
700	62
800	67
900	62
1000	88
1100	97

These figures indicate a volume photoelectric effect since dm is in all cases much larger than atomic dimensions.

In a later paper Borziak<sup>1</sup> continues the above investigation by determining the refractive index,  $n$ , and the absorption index,  $k$ , (i.e. the real and imaginary parts of the so-called "complex refractive index"). These values for the semitransparent photocathode are given in the following table.

$\lambda, m\mu$	$n$	$k$
420	2.0	0.8
500	1.9	1.0
600	1.7	0.8
700	1.8	0.6
800	1.9	0.4
900	2.0	0.3
1000	2.1	0.2
1100	2.2	0.1
1200	2.3	0.1

From these constants Borziak concludes that the course of the photoelectric yield as a function of wavelength does not parallel the total light absorption within the film. Since the quantum yield is low (about 0.1%) he concludes that only a small proportion of the light absorption is

effective in the production of photoelectrons. As has been previously pointed out in Section 1.43, Borziak also studied wedges of  $\text{Cs}_2\text{O}$  on glass without silver. In this case also the absorption of light by the film did not parallel the photoelectric current as a function of wavelength. The situation can best be summarized in the words of the author (in translation), "From this (the above) it follows that the basic optical absorption, determined by optical constants, is not photoelectric in the given cases. On it is imposed a photoelectric absorption, indirectly shown through the photoeffect, which is considerably smaller in intensity. Consequently the concentration of centers, photoelectrically absorbing light, which are probably of an admixture nature, are small, while for the oxygen-cesium photocathodes (without silver) the photoelectric absorption at the spectral maximum is the natural absorption of the basic substance of the film". The similarity to the work of Kluge is evident.

The implication that impurities constitute the source of photoelectric absorption in silver-oxygen-cesium photocathodes is certainly plausible and agrees with much indirect evidence. The implication that photoelectric absorption in  $\text{Cs}_2\text{O}$  is an intrinsic property of the perfectly pure and well-ordered solid seems to us to be far from proven.

Because the spectral sensitivities of  $\text{Cs}_2\text{O}$  films are so different from those of silver-oxygen-cesium cathodes, Borziak states that it cannot be accepted, without direct proof, that the cesium oxides are the same in the two types of cathodes. (In Section 4 of the present report an unambiguous proof is given that a silver-oxygen-cesium photocathode contains  $\text{Cs}_2\text{O}$  as the major constituent.)

In view of the work of Borziak and Margulis it seems obvious that the theory of Sayama needs revision. The optical constants for semitransparent cathodes are not the same as for silver. Nevertheless it is possible that Sayama's proposal that colloidal silver grains constitute a source of photoelectrons may be correct. Isolated silver atoms distributed through the lattice might constitute another such source, and other impurities or electrons trapped at lattice defects may constitute still another. The precise source is still unknown. Some reasonable explanation of the low work function is still required.

The optical constants of the semitransparent photocathode are far from those of quartz and hence the assumption of Ives and Olpin is, in this respect, wrong. In view, however, of the fact that the thickness used in calculation was adjusted to provide the best agreement with experiment, it seems possible that this factor is not of decisive importance. The principal conclusions of Ives and Olpin are, in fact, rather well substantiated despite the rough approximations involved.

From the above work the following conclusions are reached:

1. Thin film photocathodes of graded thickness can be prepared which behave like homogeneous films with respect to the reflection and transmission of light.
2. The electromagnetic field in a thin layer at the cathode surface is responsible for the production of photoelectrons.
3. The thickness of the layer from which photoelectrons are produced is roughly 9% of the wavelength of the illuminating radiation.
4. The radiation absorption which is responsible for photoelectron production is such a small proportion of the total radiation absorption that it is not clearly marked in transmission curves determined for semitransparent cathodes.
5. The photoelectric yield from  $\text{Cs}_2\text{O}$  films has a spectral sensitivity quite different from that of semitransparent photocathodes and hence silver is involved in the process of photoelectron production. The silver referred to is that which is finely dispersed through the photocathode. Other impurities, including cesium, may also be involved. The experiments do not establish that silver is the source of photoelectrons but it affects the process in some way.

It is difficult to appraise critically the above work. Several questions do arise, however, which it seems worthwhile to mention. The first of these concerns the thickness,  $\text{dm}$ , below which the photoelectric yield begins to fall. The evident assumption is made by Borziak and Margulis that the



film remains homogeneous below this thickness. Is it established that the decline in yield is not due to the same cause as that discussed by Morozov and Butslov, i.e. particle isolation at small thicknesses? Data on silver film thickness are not given by Borziak and Margulis. However, spectral sensitivities of cathodes 62 m $\mu$  thick were measured and were found to be normal (i.e. normal in their work. Cathodes with the long wave maximum further in the infrared can be, and commonly are, prepared. These cathodes are not, however, specular reflectors.). Since the silver films were deposited at liquid air temperature, good electrical contact is to be expected even in the thinnest sections. The subsequent oxidation apparently took place at temperatures below room temperature and this may result in a homogeneous film. Cesium addition was conducted in the "usual" way which presumably means that the film was heated. This is a step which is likely to cause the thinnest film sections to break up into isolated grains. Due to the previous treatment at low temperature this might, however, be less significant than in a normal preparation. On the whole it seems possible that the rather unusual method of preparation might result in homogeneous films down to lower thicknesses than in the experiments of Morozov and Butslov. It would be more convincing, however, if the method of preparing the cathode had been discussed in more detail and this point made specifically clear.

In conclusion one other comment on the work of Borziak and Margulis seems of interest. It is essential that the wedge-shaped photocathodes should be specular reflectors. The only proof which they offer is that the theory fits the observations although the fit is not perfect. They say that the particle size must be small in comparison with the wavelength of light. At one stage in our own investigation we also considered the use of wedge photocathodes and a few were prepared. The oxidized wedges described in Part I were prepared as a preliminary to a more systematic study. We were discouraged from making an optical study, however, for the following reasons. A silver wedge was oxidized in ozone at room temperature, and on removal from the ozone atmosphere it exhibited (in reflection) what seemed to be interference colors which followed the expected lines of equal thickness. Transmission measurements were made on the film and several maxima and minima were found. However, a microscopic examination of



of the film clearly showed that it contained large particles. These were of sufficient size to be clearly visible at 440X, the sizes and shapes being clearly defined. The particle sizes varied regularly from one end of the film to the other. Another silver film was evaporated much more rapidly than that described above and was oxidized in the same way. The thickness range was the same as before, but after oxidation no interference colors were observable on superficial examination and the transmission was entirely different. This film also contained particles invisible to the naked eye but readily visible with a microscope at 440X. In another experiment a film of graded thickness was deposited on the wall of a cylindrical tube and oxidized in an rf glow discharge. In reflected light it also showed what seemed to be interference colors following lines of equal thickness. Again on microscopic examination particles were readily visible. On the other hand, after dc glow discharge oxidation of thin silver wedges to a limited degree, much less than the above films, no particles could be detected at 440X. In view, however, of the high temperature (150 to 190°C) to which the oxidized films are heated on cesium addition, we were not by any means certain that truly specular reflectors could be prepared. Hence the projected optical investigation was abandoned. Borziak and Margulis do not state whether any microscopic examination was made to establish the absence of particles whose sizes exceed the wavelength of the light. It is again possible that deposition of the silver film at liquid air temperature followed by a low temperature oxidation might produce a film with very small particle size even though the film was heated during cesium addition. This was not specifically examined, however, or at least not stated and hence the question remains. That the question is pertinent is clearly demonstrated by the work of Asao who gives in his paper a photograph of a semi-transparent photocathode taken at 444 magnification (see ref. 23, Fig. 12). Particles are clearly visible in the photograph. The questions as to particle sizes in the photocathodes apply, of course, not only to the work of Borziak and Margulis but also to other work in which specular reflection is assumed. The work of Kluge is probably an exception because very thin films on a thick silver base were used. Moreover, as we stated earlier, a proof of specular reflection was given by Kluge. There still remains a question in our minds as to whether the films were truly specular reflectors or whether they simulate specular reflectors as the result of a complicated interference phenomenon resulting from particles

whose sizes are comparable with or greater (in the thick sections) than the wavelength of light and which vary in size from the thick to the thin sections of the films. If this is the case, the optical constants obtained are averages of some type. Even if this is the case, the work is still of value but its force is somewhat reduced. In any case the work seems to be the best available on the optical properties of the photocathode. In view of the complexity of the system it is perhaps surprising that the interference pattern can be fitted even approximately over a wedge-shaped cathode with one set of optical constants. The technical difficulties involved in such experiments are obviously very great.

### 1.7 Structural Studies of Photocathodes

The problem of defining the structural features of a Cs-O-Ag cathode by physical methods presents some serious obstacles because of the chemical reactivity of the cesium oxides present. In the following paragraphs the results reported for electron diffraction, electron emission microscopy, and electron micrographic investigations are very briefly mentioned.

Uyeda, Asao, Sayama, and Kobayashi have reported the results of an electron diffraction investigation of the photocathode<sup>33</sup>. Using a specially designed electron diffraction unit, they investigated the electron diffraction pattern for a silver oxide photocathode activated by cesium. They report that the oxidized surface gave a pattern consisting of broad rings due to Ag<sub>2</sub>O. On reaction with cesium and before photoemission was observed, a very complex pattern of rings was obtained which on reaction with cesium became very diffuse. After standing for a short while the photoemission disappeared and the sharp pattern previously obtained reappeared. The spectral response of the photocathode as a function of wavelength was not reported and the results are considered only as indicative of the feasibility of an electron diffraction study. They report a plan to redesign the apparatus for a more definitive investigation.

Moriya<sup>34</sup> has investigated the photoemission of the surface formed by the reaction of cesium with an oxidized silver cathode, using the surface in an electron emission microscope with high light intensities incident on the photocathode. The sensitivity of the cathode was low,

namely 1.5  $\mu\text{A}/\text{lumen}$  for white light from a source at 2700°K. Using a 25X magnification, photographs of the electron images for white light, light of 3,000 - 4,000Å, light of  $>6000\text{Å}$ , and polarized white light were prepared. The photographs demonstrated the following:

1. For light of 3000 - 4000Å the electrons are emitted uniformly over the entire surface.
2. For white light the emission occurs predominantly from minute areas.
3. For light of greater than 6000Å the electron emission arises from select sites of varying size present on the photo surface.
4. The emission for polarized light was independent of the orientation of the electric vector. The wavelength range for the polarized light was not specified.

The results clearly demonstrate that the photo-emission in the range of wavelengths greater than 600  $\text{m}\mu$  is the result of the presence of a polypatch surface having a low work function. A detailed study with the emission electron microscope of surfaces as a function of wavelength and conditions of preparation would certainly be of value in establishing the structure to be associated with various surfaces.

Friner and Ginititskaya<sup>25</sup> have reported preliminary results for an electron microscopic study of the structure of the Ag-O-Cs cathode. In this investigation the surface structure of Ag-O-Cs cathodes with a sensitivity of 20  $\mu\text{A}/\text{lumen}$  was examined using an evaporated quartz replica technique. In every cathode having a high sensitivity a developed relief prevails, with dimensions of unevenness of the order of 200 - 600Å, and a greater uniformity than in a less sensitive cathode. Together with the developed relief there exists in individual sections a grainy structure which to a degree resembles the backing structure. The developed relief in the case of the Cs-O-Ag cathode was observed only after treating the oxide surface with cesium vapor and if the silver base has been appreciably oxidized.

It is evident from the above discussion that definitive results have not been obtained in the structural investigations. This may be due to the fact that it is not particularly easy to prepare highly infrared-sensitive photocathodes even under the most favorable conditions. When this preparation is combined with a highly complicated technique, such as electron diffraction, in equipment for which there is little background experience, then the difficulties are greatly multiplied. As the result of these considerations we have decided to approach the problem in a different way. The use of x-rays for the study of the cathode seemed at first to be unsatisfactory. Illumination, at normal incidence, of semitransparent cathodes prepared on a thin glass base was not very successful because the amount of material in the x-ray beam is too small to give a satisfactory diffraction pattern. This defect was overcome, however, by sealing a piece of razor blade into a phototube which had attached to it a thin walled capillary of small bore. After the photocathode had been prepared a sample could be scraped from its surface into the capillary by manipulating the razor blade with a permanent magnet. The phototube was then placed in an x-ray powder diffraction camera in such a way that the x-ray beam struck only the protruding capillary containing the powder sample. Fairly good powder diffraction photographs could thereby be obtained (see Section 4). This method has the following advantages: (1) the method of tube preparation does not have to be changed, (2) by scraping a considerable area of surface an adequate sample can be obtained without breaking the vacuum, (3) a well-developed technique (x-ray diffraction) can be used without modification of equipment. This method has met with some success (see Section 4).

### 1.8 Miscellaneous Experiments

We note, in passing, a few fragmentary pieces of work on the electrical conductivity of photocathodes and also some researches on silver films.

The electrical conductivity of silver films has been studied by Morozov and Butslov<sup>24</sup>. They found that silver films deposited on a substrate at liquid air temperatures were highly conducting even when very thin, 98-95% transmission ( $0.5 - 1.0 \mu\text{g}/\text{cm}^2$ ). When evaporated onto a substrate at  $300^\circ\text{C}$ , however, films of considerably greater thickness ( $25 - 30 \mu\text{g}/\text{cm}^2$  at white light transmissions

of 4 - 5%) were required in order to establish electrical conductivity. It was also noted that silver films evaporated at room temperature may change rapidly in conductivity, sometimes by several orders of magnitude within a few seconds. Morozov and Butslov also measured the electrical conductivity of photocathodes at various stages of processing. The following figures for the resistances at various stages are of some interest:

original silver film	45.5 ohms/cm <sup>2</sup>
after oxidation	>10 <sup>8</sup> ohms/cm <sup>2</sup>
after cesium addition	86.5 ohms/cm <sup>2</sup>
after evaporating additional Ag	43.5 ohms/cm <sup>2</sup>
after heat treatment to maximum emission	29.2 ohms/cm <sup>2</sup> .

They note that resistance after cesium addition is variable and may be ten times as great as that of the original silver film. They infer, in agreement with Asao, that Cs<sub>2</sub>O is a semiconductor.

Kobayashi<sup>36,37</sup> has studied the conductivity of Cs<sub>2</sub>O films and also of photocathodes activated with Sb, Bi, Cu, and Ag. In the former case a very peculiar behavior was observed which suggests that phase transitions accompanied changes in temperature. The results are difficult to interpret.

By far the most extensive and definitive work on thin silver films is that of Sennett and Scott<sup>38</sup>. By electron microscopic examination of films of graded thickness they were able to show beautifully the grain merging which occurs as the film thickness increases. The effects of evaporation rate and of temperature of the substrate were also treated. Transmission and absorption by silver films was also studied as a function of wavelength. This extends the original work by Hass<sup>39</sup> who was apparently the first to demonstrate by electron microscopic examination that the optical and electrical anomalies of thin silver films are probably due to the unusual state of aggregation.

In a more recent study MacLauchlan, Sennett, and Scott<sup>40</sup> have demonstrated the merging of grains in evaporated silver films by making observations on the same film section at each of several stages in the evaporation.

The work of Sennett and Scott has already been referred to at some length in Part I of this report

series, so it will not be further discussed here.

### 1.9 Discussion

It is evident from the foregoing sections that considerable evidence has built up which favors a volume rather than (or, perhaps, in addition to) a surface photoelectric effect, although the precise source of photoelectrons is not definitely established. This accumulation of evidence tends to cast some doubt on de Boer's hypothesis that surface absorbed cesium atoms constitute the source of photoelectrons. It is true, however, that photoelectric yield is affected markedly by small amounts of excess cesium added at room temperature. The amounts involved are equivalent to only a fraction of a monolayer. Hence the photocathode is very likely surface sensitive (see Section 3.41). The matter is further discussed in Section 5, although definitive results have not yet been obtained.

Although marked progress has been made in the study of the cesium-oxygen-silver photocathode there is nevertheless disagreement about many vital points. Even the presence of  $\text{Cs}_2\text{O}$  in the photocathode has been questioned. It seemed important, therefore, to conclusively settle the cathode composition if possible, and hence experiments directed toward this end have been undertaken as outlined in the summary of this report. These are described in Section 4.

Many excellent experimental studies, some of which are described in foregoing sections, have been made which are definitive as far as the particular cathode studied is concerned. The very poor reproducibility in manufacture has, however, already been emphasized, and clearly shows that the process is only vaguely understood. In order to illustrate the point, we have compiled Table IV showing the position of the longwave maximum obtained by each of several investigators previously referred to. The long-wave maxima lie constantly between 700 and 800  $\text{m}\mu$ . However, Kluge<sup>26</sup> has shown that by using a roughened silver sheet the long wavelength maximum can be moved into the infrared by more than 100  $\text{m}\mu$ . Hence the photocathodes referred to in Table IV do not constitute the most infrared-sensitive cathodes available. Asao<sup>23</sup> also gives a yield curve for one cathode in which the long wavelength maximum lies further in the infrared than those listed in Table IV. Such cathodes have also been discussed by de Boer<sup>22</sup>.



TABLE IV. LONG WAVELENGTH MAXIMA

Authors	Reference	Location of long Wavelength Maximum	Year
Koller	13	750 $m\mu$	1929
Prescott and Kelly	18	$\sim$ 750 $m\mu$	1932
Asao	23	$\sim$ 700 $m\mu$ (semi-transparent)	1940
Morozov and Butslov	24	750 $m\mu$	1944
Kluge	25	750 $m\mu$	1935
Kluge	27	750 $m\mu$	1933
Ives and Olpin	29	800 $m\mu$	1934
Borziak and Margulis	32	780 $m\mu$	1948
Keller	19	750 $m\mu$	1930
Kluge	30	800 $m\mu$	1933

Note: The above values have all been corrected for lamp energy distribution.

During the course of our work we have found reason for believing that more than one type of emitting center exists in properly prepared photocathodes. One type of center gives rise to long wavelength maxima similar to those of Table IV, but others produce sensitivity considerably further in the infrared (see Sections 3 and 4). In view of this fact we might well question the applicability of much of the foregoing work to highly infrared-sensitive photocathodes. A thorough and systematic study of the photocathode with emphasis on chemical composition determinations is clearly called for. The experiments now described were conducted for this purpose.

## 2. EQUIPMENT AND TUBE FABRICATION

- 2.1 General Equipment
  - 2.11 Vacuum Systems
  - 2.12 Oven System of Tube Fabrication
  - 2.13 Spectral Response Measurement
- 2.2 Cesium Preparation and Flow Rate Measurements
  - 2.21 Cesium Preparation
  - 2.22 Cesium Flow Rate Measurement
- 2.3 Tube Fabrication. Non-Radioactive Tubes
  - 2.31 Massive Cathodes
  - 2.32 Semitransparent Cathodes
  - 2.33 X-Ray Diffraction Phase Identification Cathodes
- 2.4 Tube Fabrication. Radioactive Tracer Tubes

## 2. EQUIPMENT AND TUBE FABRICATION

As stated in the introduction, the experimental studies can be divided into four groups. (1) A systematic study of the development of thermionic and photoelectric emission as cesium is continuously added to phototubes. (2) Cathode composition determinations by means of a radioactive cesium tracer. (3) Identification of cathode constituents by x-ray diffraction. (4) A considerable group of miscellaneous experiments undertaken to (a) gain experience in cathode preparation, (b) answer specific questions relating to cathode preparation, and (c) test out ideas arising from (1), (2), (3) above. It seems more pertinent in a final report to organize the discussion in terms of the phenomena encountered rather than in terms of specific experiments. Hence the various methods of cathode preparation and testing are described in the present section so as to avoid needless repetition in subsequent sections.

The discussion of tube preparation is organized as follows. Section 2.1 is devoted to a description of the general equipment used to prepare and characterize the photosurface. Section 2.2 includes a discussion of the techniques by which the cesium for the photosurface was prepared as well as a discussion of the cesium flow rate through small bore capillaries. In Section 2.3 the methods used for the preparation and characterization of the nonradioactive cesium phototubes are discussed. The preparation of radioactive cesium tracer photocathodes is discussed in Section 2.4.

### 2.1 General Equipment

The apparatus and techniques which have been largely used in the preparation and characterization of experimental tubes are considered in this section. Furthermore, at appropriate places, the conditions used to specify the emission characteristics of photosurfaces, discussed in the following sections, are defined. The discussion has been organized using the following sequence of topics: (1) Vacuum systems, (2) oven system of tube fabrication, and (3) spectral response measurement.

#### 2.11 Vacuum systems

As described in the silver oxidation report (Part I of this series), two differently designed high vacuum systems have been used in the preparation of the experimental phototubes. System I has been used in the preparation of

nonradioactive cesium massive and semitransparent cathodes (experimental groups 1, 3, 4 above), and was consequently designed for convenient and rapid preparation of experimental tubes. System II has been used to study the gross composition of the surface with radioactive cesium and consequently was designed for the precision measurement of the oxygen deposited during the glow discharge oxidation.

Vacuum system I consists of a 26-mm diameter pyrex glass manifold to which are attached by means of stopcocks the following units: a DPI GF 25W triple-stage oil diffusion pump backed by a Welch Duoseal pump, a Welch Duoseal roughing pump, a potassium permanganate pellet oxygen source, and a Drierite tower exit to the atmosphere. Three vacuum gauges were used to measure the pressure in the system; namely, a calibrated micro Pirani gauge for oxygen pressures in the range 1.0 to 0.4mm Hg, a Cenco thermocouple gauge unit for the range 400 to 1 micron, and a DPI-VG1A ionization gauge unit for the pressure range below  $6 \times 10^{-4}$  mm Hg. The total volume of the system was 1.0 liter.

The white light transmission values of semitransparent cathodes prepared on vacuum system I were measured using an S-4 photosurface and a GE-82 6CP bulb light source operated at 6.0 volts. The current from the photocell was passed through an Ayrton shunt and measured with a No. 3402 HH Rubicon galvanometer with a sensitivity of 0.006  $\mu$ a/mm. This shunt-galvanometer combination was also used to measure the thermionic emission and white light sensitivity of experimental tubes fabricated on the manifold. In this case, a collecting voltage of 180 volts was used. It was not possible with this unit to establish during tube fabrication the voltage dependence of the observed emission currents.

Vacuum system II consisted of an 18-mm diameter pyrex glass manifold to which were attached by means of stopcocks the following units: a triple-effect liquid air trap which was connected to a two-stage mercury diffusion pump backed by a Welch Duoseal pump, a micro Pirani calibration bulb which formed a shunt across the vacuum stopcock to the liquid air trap, a sealed end mercury manometer in series with a calibrated bulb used to determine the volume of the system by a gas expansion method, a two-liter flask used in the calibration of the micro Pirani gauge, a Welch Duoseal roughing pump, an oxygen reservoir which was connected to the oxygen tank through a Drierite tower, and an exit tube to the atmosphere. A schematic drawing of the vacuum system

is given in Fig. 22 of the silver oxidation report (Part I). The pressure in the system was measured using (1) a micro Pirani gauge for the range 0.4 to 1.0 mm Hg, (2) a DPI Pirani gauge for the range from 400 to 1 micron, and the VG 1A DPI ionization gauge for pressures below  $6 \times 10^{-4}$  mm Hg. The characteristics of this micro Pirani gauge as well as of the one used on system I are discussed in considerable detail in Appendix 1 of the silver oxidation report (Part I of this Series). During tube fabrication on vacuum system II the determination of the volume of the system as well as a recalibration of the micro Pirani gauge were performed for each tube. The degrees of precision of these calibrations were such that the total volume was known to better than 1% and the pressure change during oxidation was determined to 1 micron. For the latter measurement the micro Pirani gauge was used in all cases.

Outgassing of the tubes attached to the vacuum systems was performed using a three-inch bore quartz tube resistance furnace. The tubes in general were outgassed at 375 - 450°C for at least two hours or until the pressure in the system was less than  $5 \times 10^{-6}$  mm Hg as measured with the VG 1A ionization gauge.

The silver oxidations were performed in system I using oxygen from the thermal decomposition of  $KMnO_4$  and in system II using commercial tank oxygen. For the dc glow discharge oxidations a nonregulated dc power supply with the output voltage continuously variable from 0 to 1500 volts was used. For the rf glow discharge oxidation a BC-375E Signal Corps transmitter was used as a source of radiofrequency power. The oxidation techniques are described in Part I of this series.

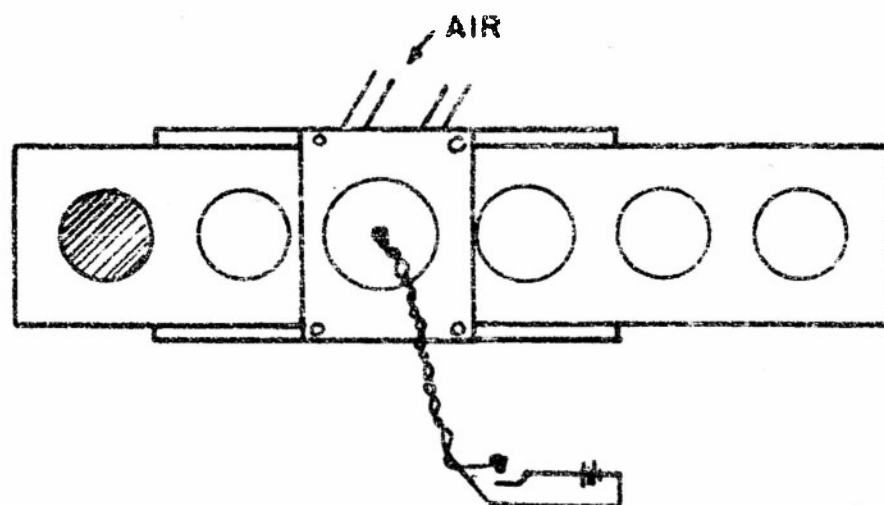
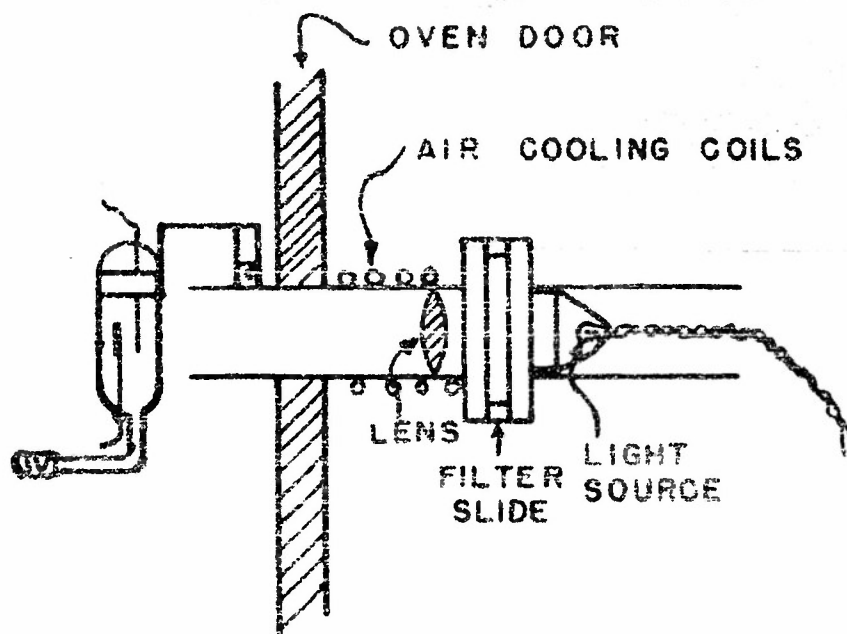
## 2.12 Oven system of tube fabrication

It was of interest to follow both photoelectric and thermionic emission during the continuous addition of cesium to an oxidized silver cathode. For this purpose the cesium source, a  $Cs_2CrO_4$ -Si pellet, is placed in a side tube attached to the phototube through a fine capillary which limits the rate of flow of cesium to the oxidized silver cathode. The side tube and its attached phototube are then placed in an oven maintained at the desired temperature, and both photoelectric and thermionic emission are measured as a function of time. The precise experimental arrangement is as follows.



The thermionic emission is followed continuously by means of a vibrating reed amplifier, to be described later, and a Brown recorder. In order to measure the photoelectric emission a hole was drilled through the front door of the oven and a length of 2 inch i.d. brass pipe inserted through the opening. The phototube is placed near one end of the brass pipe at the approximate center of the oven interior. At the other end of the brass pipe, outside the oven, is placed a tungsten filament incandescent lamp, and a series of infrared filters. The filters are mounted on a brass plate,  $\frac{1}{2}$  inch thick,  $2\frac{1}{2}$  inches wide and  $14\frac{1}{2}$  inches long. The filters are circular discs of 2-inch diameter mounted in 2-inch holes bored in the brass plate. By means of brass guides the plate containing the filters can be moved perpendicular to the axis of the 2-inch brass pipe in such a way that any filter can be interposed between the light source and the phototube. Six holes are drilled in the brass plate and five filters are mounted in it. The sixth hole is blocked off by a brass sheet so that in the sixth position the cathode is shielded from the light source. In order to better concentrate the light beam on the cathode a lens is placed between filters and cathode. A sketch which shows the mounting of the phototube, and attached side tube containing cesium, relative to the oven door is shown in Fig. 4. The lamp and filter mounting are also shown. The filters are designated by F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub>, F<sub>4</sub>, F<sub>5</sub>, while the blank position is cross hatched. A thermometer is inserted through the top of the oven so that, with the door closed, the thermometer bulb is immediately adjacent to the cathode and the temperature in the immediate vicinity of the cathode is determined. The oven used is a Cenco #95030 and the temperature is thermostatically controlled. The light source is a GE #31 bulb operated at 6.0 volts and 0.25 amps. Further details concerning the filters and current measurements are given later. The decomposition of silver oxide at 190°C has been reported previously (Part I) and found to occur at a very small rate at 190°C. For many purposes the decomposition can be ignored. Cesium vapor pressure of the cathode during tube fabrication has been studied by Sayama<sup>21</sup> and found to be negligibly small compared to the vapor pressure in the cesium source bulb, at least when the ratio of cesium atoms to oxygen atoms (Cs/O) is less than 2.6.

The experimental tube, while mounted on the vacuum system and before placing in the oven, is thoroughly out-gassed, the silver is oxidized to the desired extent, and the tube evacuated to less than  $10^{-5}$  mm Hg. The cesium chromate-silicon pellet mounted in a side tube which is connected to the phototube by a capillary of known size,



**FIG. 4 - SPECTRAL DEVICE ON OVEN**

is then fired by high frequency induction heating. After the experimental phototube is sealed off the vacuum system, it is mounted in the oven as shown in Fig. 4. The flow rate of cesium into the tube is predetermined by the capillary size and the partial pressure of cesium at the temperature of the oven. This experimental arrangement is particularly convenient since the cesium addition can be effectively stopped by placing a piece of moist cotton on the cesium bulb. This operation reduces the vapor pressure of cesium to a low value and the resultant flow rate for the capillaries used was less than a monolayer of cesium on the cathode every five minutes. In the discussion of experimental results the designation "Cs cool" is used to describe this operation. It is obvious that temperature control is impaired if the cesium source is cooled frequently. Nevertheless, this procedure has been of considerable value in the study of photocathodes, and as long as allowance is made for temperature changes, useful information has resulted.

For the measurement of the thermionic and photoelectric emission during the fabrication step the vibrating-reed amplifier Brown recorder unit used in the spectral response measurements was utilized.

A switching unit was constructed so that the input resistance to the vibrating-reed electrometer is variable from  $10^2$  to  $10^8$  ohms. This arrangement permits direct recording of currents from  $4.55 \times 10^{-9}$  to  $4.2 \times 10^{-4}$  amperes full scale recorder deflection. The standard convention adopted for recording the emission data is in units of millimeters of recorder deflection on the  $10^2$  ohm input resistor range for which the sensitivity is  $0.015 \mu\text{A/mm}$  deflection. In terms of the  $10^2$  range units the following current ranges are available: X 0.001, X 0.01, X 0.1, X 0.5, X 1.0, X 2.0, X 5.0, X 10.0, X 50.0, and X 100. These are the factors by which a recorder deflection on a given scale, must be multiplied in order to convert to the  $10^2$  range.

Initially the experimental tube voltage supply was restricted to the values 67.5, 135, 202.5, 270, and 337.5 volts. After a short period of operation it became apparent that this set of voltages was too limited. To more fully establish the emission characteristics during processing it is desirable to measure the emission at both higher and lower voltages. Consequently a two selector switch voltage supply unit was constructed. With this unit the emission current can be measured at 0.0, 7.5, 15.0, 22.5, 45, 67.5, and 120 volts with one set of selector switch positions,

and with the second selector switch voltage from 0 to 607.5 volts in 67.5 volts steps can be added. The total voltage range for emission measurements thus available is from 0 to 742.5 volts. With the variable voltage supply it is readily possible to establish whether the observed current is a thermionic emission or merely a conduction leakage current between the electrodes. The voltage dependence of thermionic and photoelectric emission can also be studied. From the variation of the photoelectric emission with voltage it is readily possible to establish whether or not the tube is "gassy". In addition, with a reversing switch in the input line circuit from the experimental tube it is possible to study photoelectric and thermionic emission by the anode during fabrication. By means of reversing the polarity, i.e. making the photosurface the anode, it is easy to distinguish between an ohmic conduction current, arising from a conducting film on the tube envelope, and a genuine thermionic emission.

The photoelectric emission of the cathode during cesium addition is measured by illuminating the cathode with the light from a GE #31, 6.2-volt bulb, passed through a sequence of filters as previously explained (see Fig. 4). During cesium addition the tube is periodically illuminated by the light transmitted through the filters, and the photoelectric current is measured on the Brown recorder with the thermionic emission as the base line. With the light source used, the photoelectric response is always sufficiently large to be readily measured.

The five filters used in the investigation are as follows:

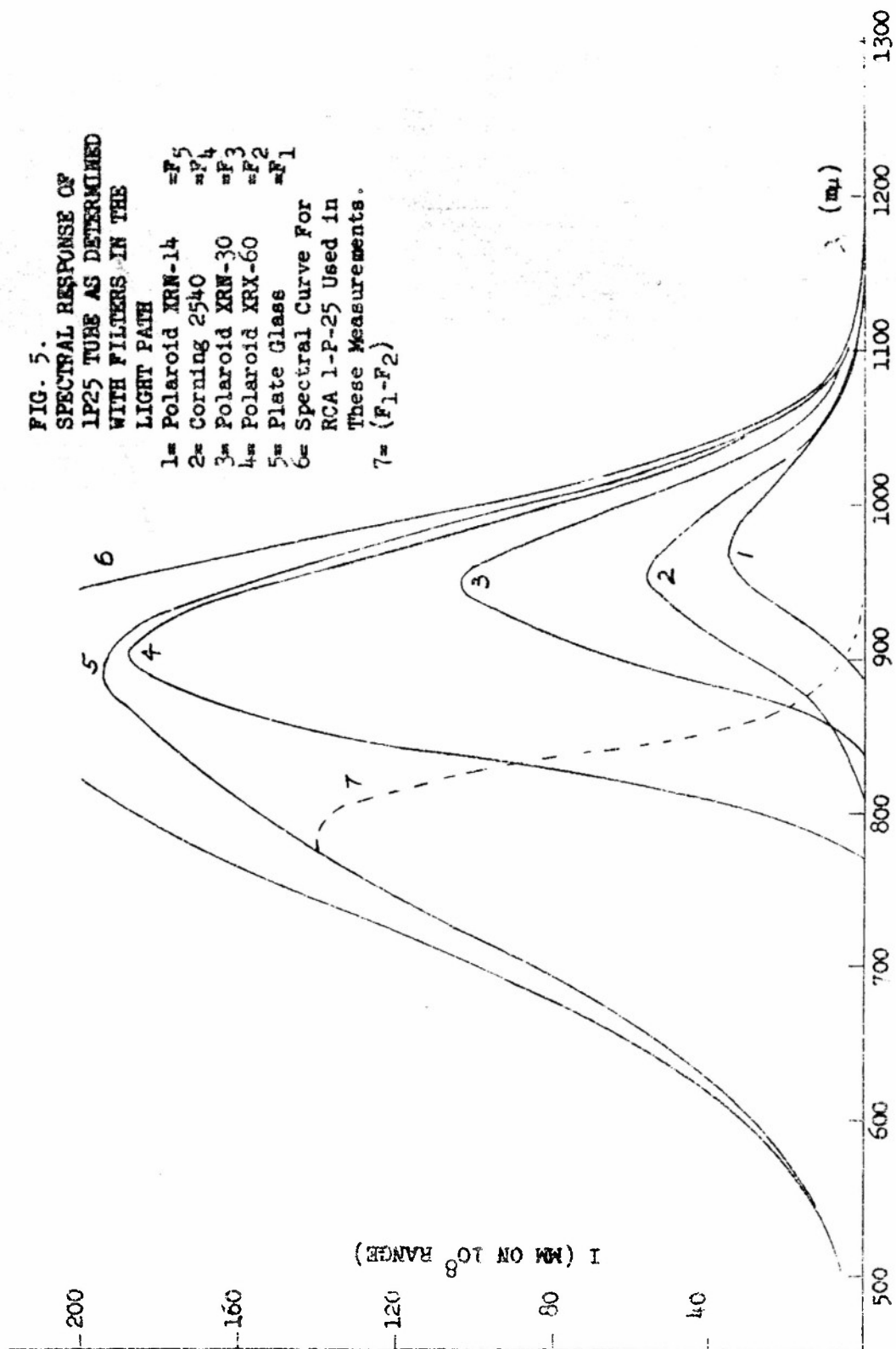
- F<sub>1</sub> - clear glass
- F<sub>2</sub> - polaroid XRX-60  $\lambda > 775 \text{ m}\mu$
- F<sub>3</sub> - polaroid XRN-30  $\lambda > 830 \text{ m}\mu$
- F<sub>4</sub> - Corning 2540-  $\lambda > 800 \text{ m}\mu$
- F<sub>5</sub> - polaroid XRN-14  $\lambda > 880 \text{ m}\mu$

The photocurrents obtained by illumination through these filters are designated in the following text as F<sub>1</sub>, F<sub>2</sub>... responses respectively.

The spectral response of a 1P25 tube determined by passing the light beam from the Beckman DU spectrophotometer through the various filters is shown in Fig. 5. In this figure it is worth noting that the F<sub>2</sub> filter increases the infrared response beyond 775 m $\mu$  without introducing a large absorption correction beyond 900 m $\mu$ . In addition, a cathode which has an appreciable response beyond 900 m $\mu$ .

FIG. 5.  
SPECTRAL RESPONSE OF  
1P25 TUBE AS DETERMINED  
WITH FILTERS IN THE  
LIGHT PATH

- 1= Polaroid XRN-14 =F<sub>5</sub>
- 2= Corning 2540 =F<sub>4</sub>
- 3= Polaroid XRN-30 =F<sub>3</sub>
- 4= Polaroid XRX-60 =F<sub>2</sub>
- 5= Plate Glass =F<sub>1</sub>
- 6= Spectral Curve For  
RCA 1-P-25 Used in  
These Measurements.
- 7= (F<sub>1</sub>-F<sub>2</sub>)



must have a fairly large  $F_5$  response. The difference ( $F_1 - F_2$ ) is a rather direct measure of the response of the photosurface for wavelength appreciably shorter than 850 m $\mu$ . This is illustrated by the dotted curve in Fig. 5. The transmission curves for the filters calculated from the spectral response data are shown in Fig. 6.

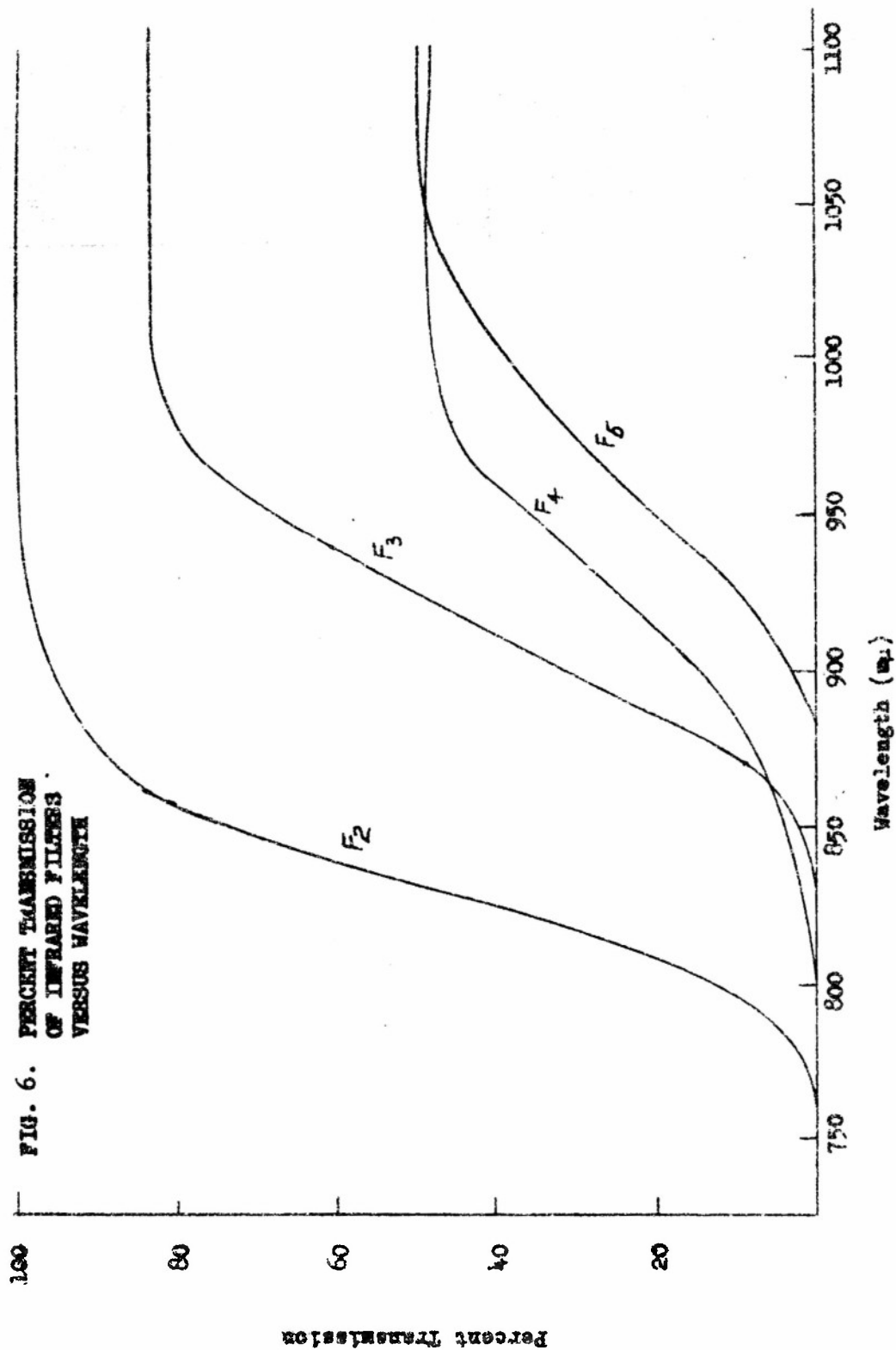
### 2.13 Spect response measurement

In order to characterize the experimental photosurfaces it is necessary to measure the spectral response after each processing operation. This requires a convenient and rapid method of recording the response curves.

The apparatus used in the measurement of the spectral response of phototubes is illustrated in Fig. 7. A Beckman DU spectrophotometer is used as a source of monochromatic radiation. The sample holder and tube housing on the Beckman were replaced by a special design phototube housing which could accommodate a wide variety of tube designs. In order to reproduce the tungsten light source operating conditions a precision voltage divider was mounted across the lamp terminals, and the voltage drop across the lamp measured with a Rubicon potentiometer. The input voltage to the lamp is adjusted so that the voltage drop across the lamp is 5.00 volts. Under these conditions the uncorrected color temperature of the lamp is approximately 2400°K as determined with a Leeds and Northrup optical pyrometer. This figure is the average of four readings taken at the interior of the filament coils. The temperature is approximate since the filament supports cool the ends etc.

The output from the phototube is measured using a high input impedance vibrating reed electrometer similar to that described by Palevsky, Swank, and Shull<sup>41</sup>. This unit consists of a vacuum tube oscillator driven dynamic condenser coupled to a tuned amplifier and detector circuit. The output from the electrometer is coupled to a Brown recorder for recording the phototube current as a function of wavelength. The wavelength drum of the spectrophotometer is driven with a 4 rph synchronous motor. The electrometer sensitivity for fullscale recorder deflection (280mm) and a  $10^8$  ohm input resistor is  $5.8 \times 10^{-11}$  amp. on high sensitivity,  $4.55 \times 10^{-10}$  amp. on medium, and  $4.55 \times 10^{-9}$  amp. on low sensitivity.





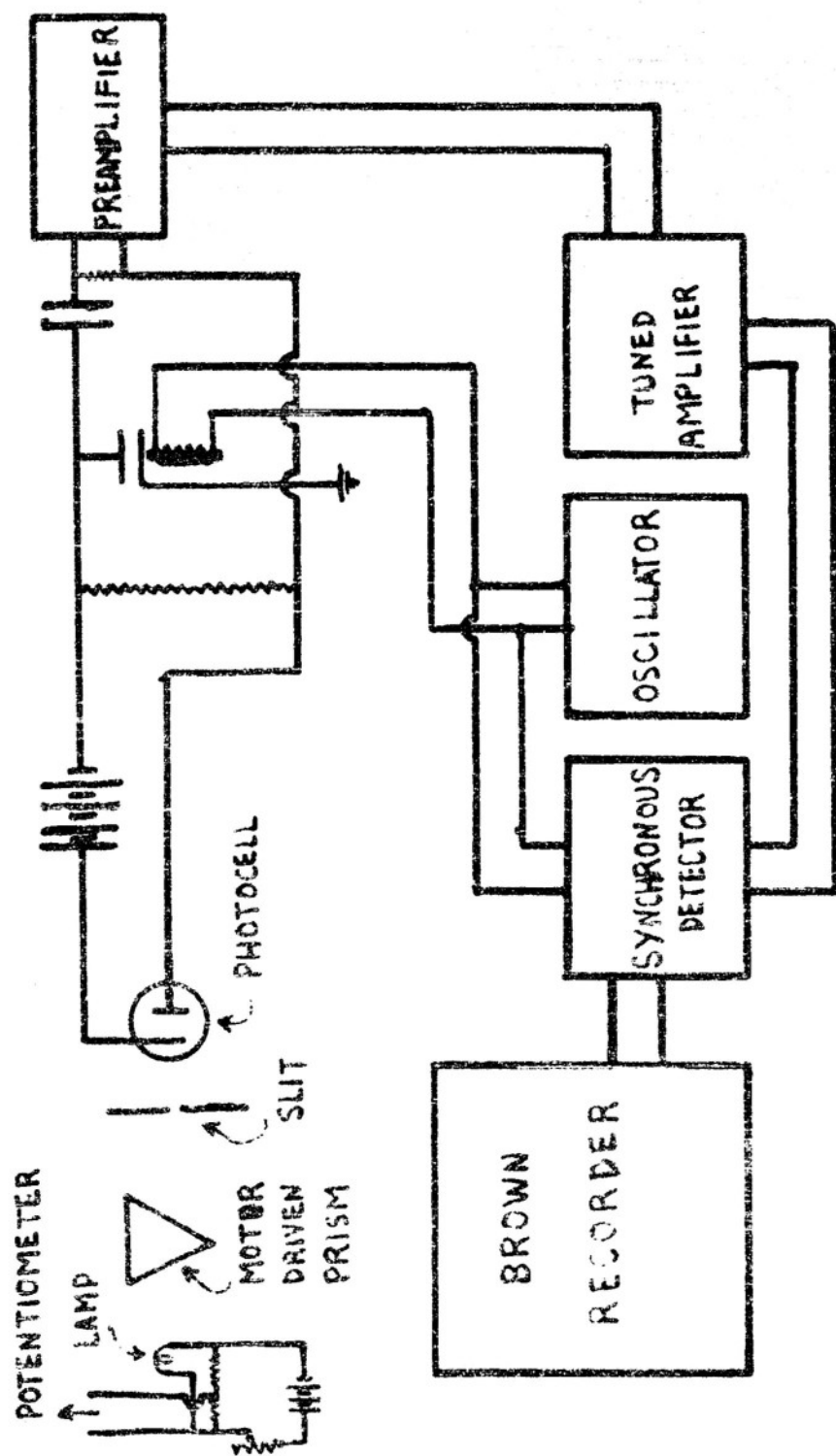


FIG. 7-APPARATUS FOR SPECTRAL CURVES

In order to provide a basis for the comparison of the spectral responses a set of standard measurement conditions was finally adopted. The conditions applying to the majority of the spectral response data reported in the following sections are as follows:

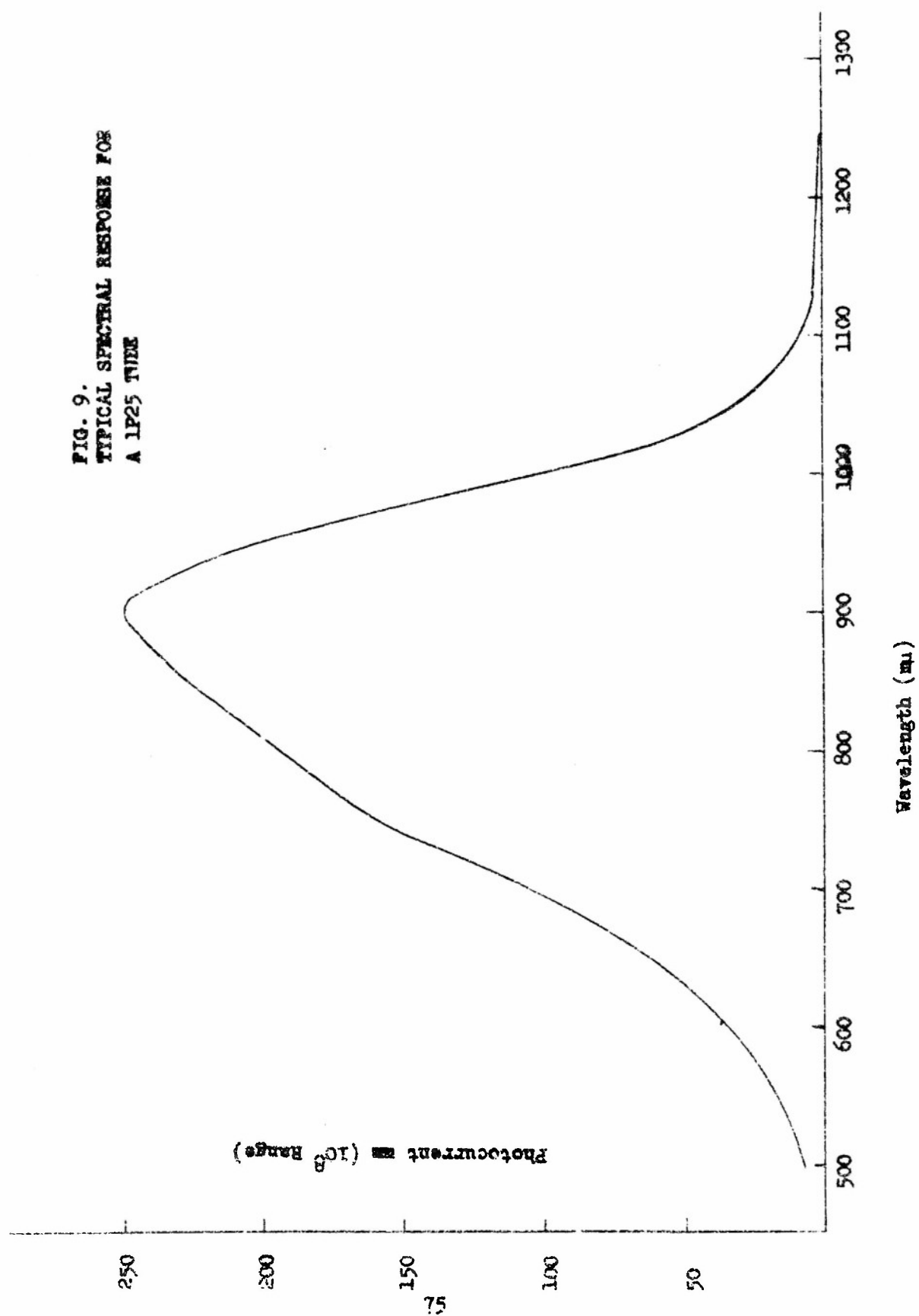
1. Light source voltage - 5.00 volts.
2. Beckman spectrophotometer slit width - 0.150mm.
3. Photoemission collector voltage - 202.5 volts.
4. Electrometer sensitivity - low.
5. Photocurrent expressed in mm. Recorder deflection with the  $10^8$  ohm input resistor.

For the low sensitivity range on the vibrating reed electrometer the sensitivity is  $1.6 \times 10^{-11}$  amperes per millimeter. In Fig. 9 is shown a typical response curve for a commercial tube (1P25) measured using the standard conditions quoted. The commercial tubes were characterized by a maximum between 890 - 940  $m\mu$  and a long wavelength limit from 1200 to 1350  $m\mu$ .

It is interesting to compare Fig. 9 with the spectral response obtained (on a different phototube of a somewhat similar type) by Gibson and Balcom<sup>42</sup> using a Beckman DU spectrophotometer. The response curve obtained by them has almost exactly the same shape as that of Fig. 6.

Since we were chiefly interested in comparing cathodes prepared under different conditions we have not corrected the spectral responses for dispersion of the monochromator nor for lamp energy distribution except, approximately, in a few instances. Such correction has a considerable influence on the shape of a spectral response curve. It proves to be the case, however, that the position of the long wave maximum usually does not change very much and the long wave limit does not, of course, change at all. The effect of lamp energy distribution on spectral response has been discussed by Koller<sup>43</sup>. In an example given by Koller the position of a long wave maximum at 800  $m\mu$  is not shifted on correction for lamp energy distribution of an incandescent source at 2400°K, which is close to the filament temperature in our own source. Approximate calculations (see Section 3.2) of our own, using the lamp energy distributions reported by others, indicate that maxima in the vicinity of 900  $m\mu$  may be shifted to shorter wavelengths by about 30  $m\mu$  and maxima at 800  $m\mu$  are also shifted to shorter wavelengths by about the same amount. Similar results for the latter case have been obtained by Ballard<sup>44</sup>. These remarks apply only to spectral response curves of "normal" shape, i.e.

FIG. 9.  
TYPICAL SPECTRAL RESPONSE FOR  
A 1P25 TUBE



those which do not depart too widely from that of Fig. 6. Abnormal spectral response curves may, of course, violate the above generalizations. Since, however, we are dealing always with closely related photocathodes the above general remarks are usually applicable and are of some use in comparing the data reported here with those of other investigators who have usually corrected for lamp energy distributions. It is worthwhile to note that on correcting for lamp energy distribution the short wavelength side of a curve such as that of Fig. 9 tends to be raised relatively more than the long wavelength region. It will be evident from the subsequent discussion that these points are not of major importance in the interpretation of results.

## 2.2 Cesium Preparation and Flow Rate Measurements

In order to prepare the Ag-O-Cs cathode it is necessary to have a convenient source of cesium as well as a method for controlling the rate of cesium addition to the tube. The methods used to obtain the cesium and to control its flow rate into a phototube are discussed in this section.

### 2.21 Cesium preparation

For the nonradioactive cesium phototubes, cesium was obtained by firing commercial  $\text{Cs}_2\text{CrO}_4$ -Si pellets (RCA code FZ607E), mounted in tantalum or nickel cups, using induction heating. The yield of cesium obtained from the pellets for the actual degassing and firing conditions used was  $4.3 \pm 0.4$  mg Cs/pellet.

For the investigation of the gross composition of the photo surface it was necessary to use  $\text{Cs}_2\text{CrO}_4$ -Si pellets containing radioactive cesium. The following procedure was used to prepare these pellets.

The cesium isotope used is  $\text{Cs}^{134}$  which has a half life of  $2.3 \pm 0.3$  years<sup>45</sup>. The decay scheme for  $\text{Cs}^{134}$  is shown in Fig. 8. The isotope was obtained from the Oak Ridge National Laboratory as a 0.2m $\ell$  solution of the chloride in water. The spectroscopic analyses given on the shipping list are as follows:

Baron-Iron	- faint trace
Aluminum	- trace
Silicon	- very weak
Magnesium	- moderate
Calcium	- very strong.

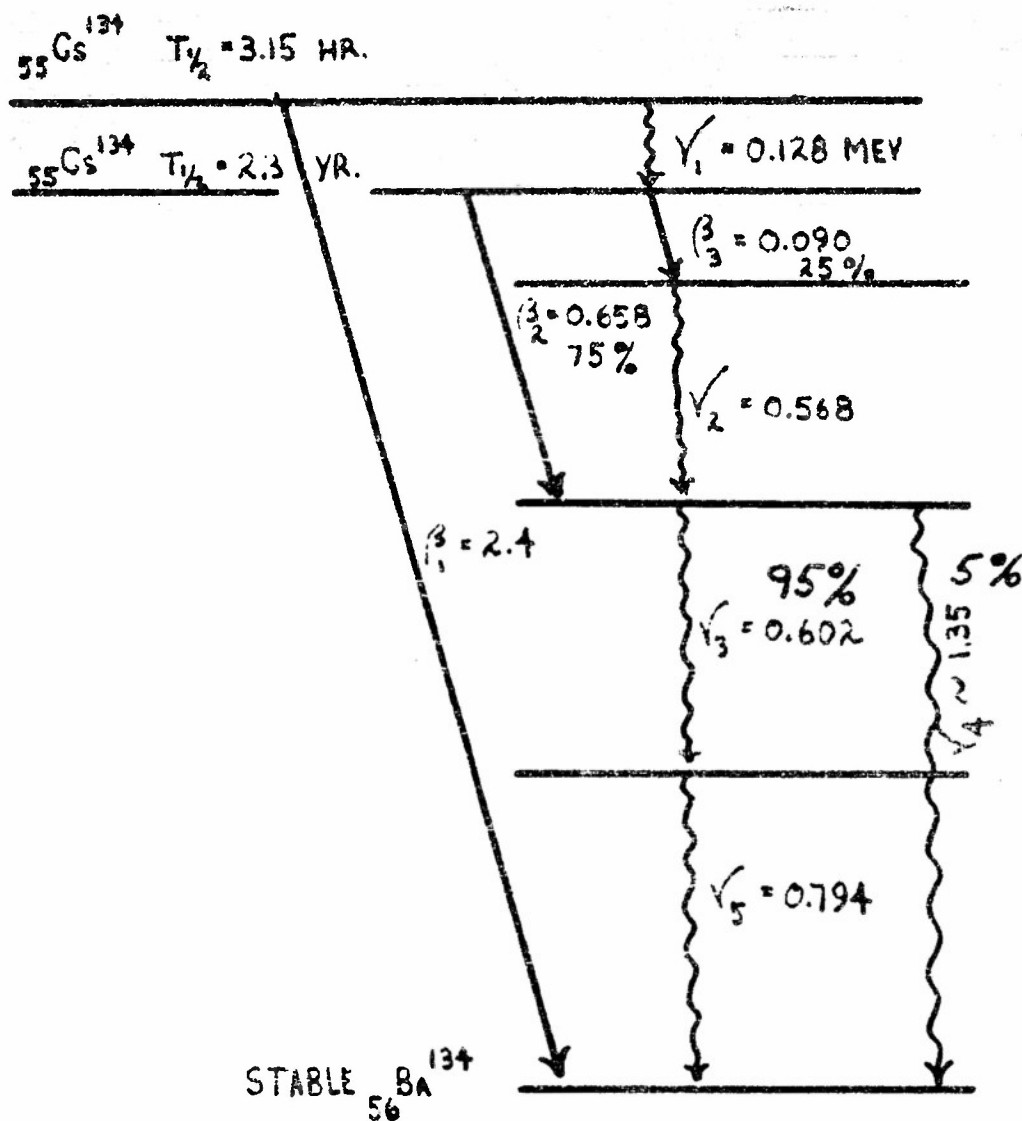


FIG. 8 -DECAY SCHEME OF  $^{134}_{55}\text{Cs}$



The 0.2 ml solution was diluted with 15 ml of 0.1 normal HCl and 1 ml of the resulting solution was removed and diluted with 100 ml of 0.01 normal HCl. The activity of the solution was then measured by removing 25 lambda (0.025 ml) of this solution and evaporating on a microscope cover glass under a heat lamp. This sample gave 14,000 counts per minute with the sample geometry described later in the section on the preparation of radioactive Cs tubes. A 25 ml sample of the above solution was then diluted to 100 ml to give a solution having about 4000 C/M per 25 lambda.

A sample of stable (i.e. nonradioactive) CsCl was weighed by difference and transferred to a 50 ml weighing bottle and 20 ml of the dilute tracer solution added to give a solution with 4000 C/M/25 lambda. After stirring, standard samples were removed for calibrating subsequent samples of unknown cesium concentration.

Solid silver chromate was now added to the solution and the solution stirred thoroughly while heating with an infrared lamp. The solution was cooled in an ice bath and centrifuged to precipitate the silver chloride and excess silver chromate. The supernatant liquor was removed and evaporated to 10 ml and again cooled and centrifuged. The supernatant liquor was then placed in a weighed centrifuge tube and the  $\text{Cs}_2\text{CrO}_4$  precipitated with acetone. The cesium chromate was washed with acetone, dried at 110°C for about five hours, and finally cooled in a desiccator.

After weighing, the cesium chromate was mixed thoroughly with an equal weight of silicon powder fine enough to pass through a 200 mesh screen. Portions of the resulting mixture were pressed into tantalum cups to form the  $\text{Cs}_2\text{CrO}_4$ -Si pellets for the tube preparation.

The yield of cesium from the pellets, on firing by induction heating, was quite variable and depended upon the degree of preliminary degassing; a non degassed pellet giving the highest yield. Yield studies for seven pellets prepared by the above procedure, but without radioactive cesium tracer, gave the following results: 32, 21, 20, 10, 7, 4.5, and 0.1% yield. The pellets containing radioactive cesium were fired under those conditions which gave a yield of approximately 20%. No difficulties associated with the production of insufficient cesium were encountered in the tracer investigations.

## 2.22 Cesium flow rate measurement

Two methods have been used to determine during processing the chemical composition of the experimental surfaces; namely, (1) the addition of excess cesium followed by a distillation technique to remove the excess, and (2) deposition of a known amount of oxygen on the cathode followed by controlled cesium addition through a capillary tube connecting the cesium source to the tube. In order to calculate the cesium flow rate into the tube it is necessary to know the vapor pressure of the cesium and the capillary dimensions, as well as the nature of the cesium flow.

The vapor pressure of cesium as determined by the positive ion method is given by the equation<sup>46</sup>

$$\log P = 9.86 - \frac{3774}{T}$$

where  $P$  is the pressure in microns and  $T$  is the absolute temperature. From this equation the vapor pressure of cesium is calculated to be  $5.14 \times 10^{-2}$  mm Hg at  $190^\circ\text{C}$ ,  $8.72 \times 10^{-3}$  mm Hg at  $150^\circ\text{C}$ ,  $1.74 \times 10^{-6}$  mm Hg at  $25^\circ\text{C}$ , and  $3.0 \times 10^{-12}$  mm Hg at  $-68^\circ\text{C}$ . It is to be noted that this pressure is in terms of cesium atoms, the possible presence of  $\text{Cs}_2$  molecules is not considered.

It is well known that the dependence of the rate of flow of a gas through a capillary on the capillary dimensions depends on the ratio of mean free path to capillary diameter. If this ratio is large, the Knudsen equation applies while if the ratio is small the Poiseuille equation applies. The equation describing the flow in the first case will be referred to as the molecular flow equation in the following text. When the mean free path and the capillary diameter are nearly equal neither of these equations is accurate. In this case another relation, referred to hereafter as the intermediate pressure flow equation, must be used. Using the data of Estermann, Forier and Stern<sup>47</sup> the mean free path for cesium in the saturated vapor at  $190^\circ\text{C}$  has been calculated and found to be approximately 0.06 mm. This is not large in comparison to the capillary diameters which have been used and hence the flow equation valid at intermediate pressures should apparently be used in the calculation of flow rates. For future reference we note that the mean free paths at one micron pressure are 0.266 cm and 0.290 cm at  $150^\circ\text{C}$  and  $190^\circ\text{C}$  respectively.

Although the Knudsen equation may not be accurately applicable it has nevertheless been used for approximate calculations. A form of this equation suitable for numerical calculation is as follows (see ref. 46 p.96).

$$n = 3.638 \times 10^{-3} K A \sqrt{\frac{T}{M}} \frac{\Delta P}{RT} \text{ moles/sec.} \quad (1)$$

The symbols are defined as follows:

- $K = 1/(1 + 3L/8a)$
- $L$  = capillary length in cm
- $a$  = capillary radius in cm
- $\Delta P$  = pressure drop along capillary in microns
- $A = \pi a^2$
- $M$  = molecular weight of gas
- $R = 62.36 \text{ (mm)(liter)(deg}^{-1}\text{)(mol}^{-1}\text{)}$
- $T$  = temperature in degrees absolute
- $n$  = flow rate in moles per second.

When the atomic weight of cesium and the gas constant,  $R$ , are substituted into this equation we obtain for the flow rate of cesium in moles per second

$$n = 15.98 \times 10^{-6} \frac{a^2 K \Delta P}{\sqrt{T}} \quad (2)$$

It is to be noted that the above equation differs from the usual Knudsen equation because of an end correction. When  $L/a$  is large the equation reduces to the Knudsen equation. In our experiments  $L/a$  is large enough so that the end correction is actually negligible.

In the intermediate pressure region where the mean free path is comparable with the capillary diameter the equation which applies is as follows (see ref. 46 p. 112):

$$n = \frac{\Delta P a^3 10^{-6}}{2 RT} \left\{ \frac{0.5236}{\eta} a P_a + 3.048 \times 10^4 Z \sqrt{\frac{T}{M}} \right\} \quad (3)$$

- where
- $n$  = flow rate in moles per second
  - $P_a$  = average pressure (microns) along capillary.  
This is equal to  $\frac{1}{2} \Delta P$  if the downstream pressure is negligible as is the case in our experiments.
  - $Z = \{1 + 2.507(a P_a / L_1)\} / \{1 + 3.095 a P_a / L_1\}$
  - $L_1$  = mean free path at one micron pressure.
  - $\eta$  = viscosity of gas, poise.

The remaining symbols are the same as in the previous equation. All pressures are in microns. Note that  $\lambda/a$  is assumed to be so large in comparison to unity that the end correction can be neglected.

As stated above, the molecular flow equation (1) is only applicable when the mean free path is large in comparison to the capillary diameter. Since this condition is not satisfied at 190°C the intermediate pressure flow equation (3) should actually be used. This requires, however, a value for the viscosity which is not known with any assurance. Moreover, the proportion of  $\text{Cs}_2$  in the vapor is also unknown. On this account it seemed essential to determine by direct experiment the amount of cesium flowing through the capillary per unit time. In this undertaking we were assisted because in the experiments at 190°C the same capillary was used over and over in a number of experiments. The same was true of another capillary used at 150°C. Hence the flow rates were determined by experiment for two capillaries of the same bore as the above two. It was desirable to conduct these experiments in a manner as nearly similar as possible to that in which the capillaries were used. Hence the phototube envelopes were replaced by glass bulbs containing glass cooling coils through which cooling water could be circulated. These bulbs were sealed to the capillaries through lengths of glass tubing, of large bore, which were long enough so that the bulbs with cooling coils projected outside the oven when the capillary and its attached tube containing  $\text{Cs}_2\text{CrO}_4\text{-Si}$  pellets were inside the oven at the same position as in actual experiments. The bulb and capillary were then evacuated in the usual way and the  $\text{Cs}_2\text{CrO}_4\text{-Si}$  pellet fired with an induction heater just as in the preparation of a phototube. The capillary with its attached bulb containing cesium was then placed in the oven in its usual position with the cooling bulb projecting out of the oven through the hole in the door. The oven was heated in the same manner as in the preparation of a phototube and the cesium which passed the capillary condensed on the cooling coils outside the oven. The flow was continued for a sufficiently long period to collect a sample large enough for analysis. At the end of the experiment the capillary was sealed off from the cooling bulb. The latter was then cracked open and distilled water added to it. Chemical reaction occurs at this step, cesium being converted to cesium hydroxide quantitatively. The quantity of cesium was then determined by titration using a standard solution of hydrochloric acid. The normal error in such an analysis is about 0.2%. The results obtained in two such experiments, using the two capillaries mentioned above, are summarized

in Table V. It is found that the flow calculated by the molecular flow equation at 190°C is 13% greater than the observed, and at 150°C is 6.6% higher. To compute a value for the flow rate by the intermediate pressure equation, the 190°C data were first used to compute the viscosity of cesium at 190°C. The viscosity at 190°C was corrected to 150°C assuming the viscosity to be proportional to the square root of the absolute temperature. This value of the viscosity was then used to calculate the cesium flow rate at 150°C. The resulting value for the flow rate was  $8.58 \times 10^{-8}$  moles/min. which is 0.9% less than the observed value. The coefficient of viscosity calculated at 190°C is  $51.5 \times 10^{-5}$  poise and at 150°C  $49.2 \times 10^{-5}$  poise. These values are, of course, not highly accurate.

The results of these experiments suggest that, for the capillaries used, the cesium flow rate is best determined by the intermediate pressure flow equation (3). The calculated coefficients of viscosity are of the order of magnitude to be anticipated for an atomic species such as cesium. It is interesting that it is not necessary to suppose that  $\text{Cs}_2$  molecules are present in the vapor in order to account for the observed flow rates.

A number of experiments on photocathodes were performed before the calibration described above was made. In these cases the molecular flow equation was used to compute the amount of cesium entering the tube envelope per unit time. Where high accuracy is not required these calculations have not been corrected. Unless the contrary is explicitly stated these approximate values are used in the following text. It is to be noted that the Cs/O ratios obtained in this way are too high by the amounts indicated in Table V.

### 2.3 Tube Fabrication. Non-Radioactive Tubes.

The design, fabrication methods, and characterization of experimental tubes are conveniently considered under two headings; namely, radioactive and non-radioactive photo-tube fabrication. The discussion of the non-radioactive tubes may be further subdivided into the following tube types: (1) Massive cathodes, (2) Semitransparent evaporated silver film cathodes, (3) cathodes for use in phase identification by x-ray diffraction. The methods which have been used to prepare and characterize these cathodes are discussed in the following subsections.

TABLE V. CESIUM FLOW RATE THROUGH CAPILLARIES

Capillary	Radius cm	Length cm	Observed Flow moles/min	Calculated Molecular Flow moles/min
A (190°C)	0.0504	5.01	$1.342 \times 10^{-7}$	$1.51 \times 10^{-7}$
B (150°C)	0.0573	2.051	$8.66 \times 10^{-8}$	$9.23 \times 10^{-8}$

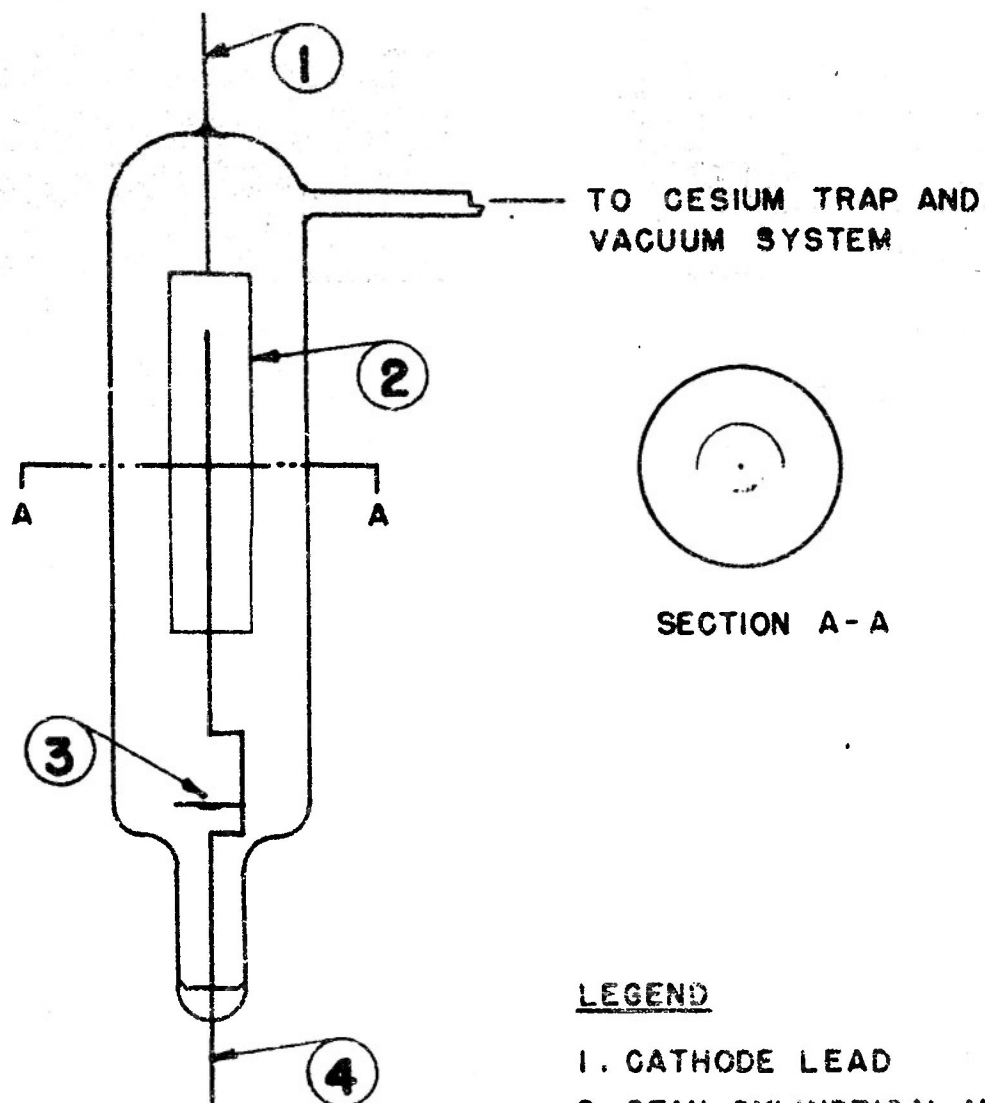


### 2.31 Massive cathodes

Three types of massive cathodes have been used for the following three purposes. (A) One type of massive cathode has been used in the study of photosurfaces containing  $\text{Cs}_2\text{O}$ . It is known (see Section 1.1) that if excess cesium is added to silver oxide a suboxide of cesium is formed. On heating this suboxide at  $190^\circ\text{C}$  for long periods of time cesium can be distilled out of it and  $\text{Cs}_2\text{O}$  forms as the end product. This procedure has been used in the preparation of cathodes containing  $\text{Cs}_2\text{O}$ , the excess cesium being distilled into a cold trap. An example of a tube, PT24c, prepared in this way is given in Section 3.2. (B) Other massive cathodes have been prepared by introducing cesium into a tube containing oxidized silver while the tube is still attached to the vacuum line. Some cesium is, of course, pumped out during this process. Since, however, the measured thermionic emission serves as a control it is nevertheless possible to continue this process until maximum thermionic emission is obtained and thereby to prepare an infrared-sensitive cathode. A procedure similar to this is used in the manufacture of semitransparent photocathodes and we have tested the procedure using massive cathodes. The results obtained for several cathodes are given in Section 3.42. The method of tube preparation is given below. (C) In the third series of experiments (see Section 3.1) a third type of cathode was used in the study of both thermionic and photoelectric emission during the addition of cesium to an oxidized silver sheet. In these experiments the cesium flow rate was limited by fine capillaries as described in the previous section. The tube designs and the details of the preparation methods are described below for each of the above types A, B, C.

The tube design used in series (A) above is shown in Fig. 10. The tube consists of a semicylindrical silver sheet cathode with a concentric anode lead wire. The  $\text{Ca}_2\text{CrO}_4\text{-Si}$  pellet is mounted in the end of the tube containing the anode lead wire so that it can be conveniently fired by induction heating. A cold trap is mounted in the exhaust line to the vacuum system. The fabrication procedure for tube PT24c, which is discussed in Section 3.2, is as follows:

1. Etch Ag cathode with 1:1 nitric acid, rinse with distilled water, dry at  $130^\circ\text{C}$ .
2. Assemble tube and seal to vacuum system.
3. Degas at  $300^\circ\text{C}$  to a pressure of  $1.5 \times 10^{-6}$  mm Hg.
4. Oxidize with a glow discharge in oxygen to the first order gun metal blue color. Pressure change  $\approx 40$  mm (in a liter system) at  $27^\circ\text{C}$ .
5. Evacuate tube to  $P \leq 1 \times 10^{-5}$  mm Hg.



LEGEND

- 1. CATHODE LEAD
- 2. SEMI-CYLINDRICAL MASSIVE SILVER CATHODE
- 3. CESIUM CHROMATE SILICON ACTIVATOR
- 4. ANODE LEAD

**FIG. -10**  
**MASSIVE CATHODE TUBE DESIGN PT-24-C**

6. Degas and fire  $\text{Cs}_2\text{CrO}_4$ -Si pellet using induction heating.
7. Tip off tube from the vacuum system.
8. Bake at 180 - 200°C in quartz tube furnace for definite time with the trap cooled by a dry ice-acetone mixture. The tube temperature was measured with a thermometer placed in contact with the tube opposite the cathode. Thermionic emission was measured with a Rubicon galvanometer with  $E_p \approx 29$  volts. (See Section 3.2 for results.) Cesium distilled from the cathode during baking, collects in the cold trap. The vapor pressure of cesium in the trap is  $10^{-12}$  mm.
9. Measure spectral response of the tube at room temperature using the Beckman DU spectrophotometer under the following conditions:  $E_p \approx 65$  volts, Beckman slit width = 0.32 mm, lamp voltage 4.97 - 4.99 volts, and the vibrating reed at low sensitivity.
10. Repeat 8 and 9 above for several cycles as discussed in Section 3.2.

In experiments of type (B), described above, the tube design was modified. The semicylindrical cathode was replaced by a 2.5x5 cm plane silver sheet mounted in a tantalum wire frame. The  $\text{Cs}_2\text{CrO}_4$ -Si pellet is mounted in a side tube rather than in the tube envelope. The cesium flow rate into the tube is, in part, controlled by placing a short section of approximately 1 mm capillary in the line connecting the trap of the tube. The exhaust tube is sealed directly into the tube envelope.

The procedure used in the fabrication of these tubes (type B) is as follows (see Section 3.42 for results):

1. Lightly etch Ag cathode with nitric acid, rinse with distilled water, dry at 130°C.
2. Assemble tube and seal to vacuum system.
3. Oxidize cathode with dc glow discharge in oxygen at  $\sim 0.7$  mm Hg to establish conditions for uniform oxidation.
4. Degas tube at 375 - 400°C for at least 1 hour. Final pressure  $\leq 2 \times 10^{-6}$  mm Hg. This decomposes the oxide formed in step 3.
5. Oxidize surface to desired color with dc glow discharge in oxygen at 0.7 mm Hg.
6. Evacuate tube to  $< 1 \times 10^{-5}$  mm Hg.
7. heat tube to 180 - 190°C.
8. Fire  $\text{Cs}_2\text{CrO}_4$ -Si pellet in side tube.
9. Heat cesium side tube and capillary to desired temperature using small tube furnace. By controlling the temperature of the side tube the cesium flow rate can be controlled at least approximately.

10. Discontinue cesium addition shortly beyond maximum thermionic emission.
11. After discontinuing cesium addition the thermionic emission rises to a maximum and then falls. Cool tube after thermionic emission passes this second maximum.
12. Seal off cesium source if it is not to be used as a trap for excess cesium.
13. Seal tube off vacuum system.
14. Measure spectral response using standard conditions:  $E_p \approx 202.5$  volts, lamp  $\approx 5.00$  volts, slit width  $\approx 0.150$  mm, and vibrating reed amplifier at low sensitivity.

The procedure described above is very similar to the usual procedure for the preparation of semitransparent cathodes. The major difference is the replacement of the thin silver film by a silver sheet. The massive cathode procedure has been extensively used to study the Ag-O-Cs surface because of the relative simplicity of the procedure and the ready reproducibility of general cathode characteristics.

For the experiments of type C, described above, the massive cathode design was only slightly altered. The cesium trap was replaced by a bulb containing a  $\text{Cs}_2\text{CrO}_4$ -Si pellet mounted in a tantalum or nickel cup. The large capillary previously used to control the cesium flow rate was replaced by a section of capillary having an accurately measured bore and length. The dimensions of the capillary were so chosen that the tube gross composition would reach a 2.0 (Cs/O) mole ratio after a predetermined period of time, at the fabrication temperature, with a given amount of oxygen deposited on the cathode during glow discharge oxidation. To simplify the process of choosing a capillary for a particular experiment, the bore for several lengths of different size pyrex capillary was carefully measured and a large scale graph was prepared giving the cesium flow rate calculated from the molecular flow equation (2) as a function of the fabrication temperature and the length of the capillary. The measured diameters of the capillaries used were as follows:  $2.049 \pm 0.004$  mm,  $1.143 \pm 0.002$  mm,  $0.915 \pm 0.002$  mm, and  $0.6870 \pm 0.0007$  mm.

The procedure used in the preparation and characterization of these type C cathodes (see Section 3.1) is as follows:

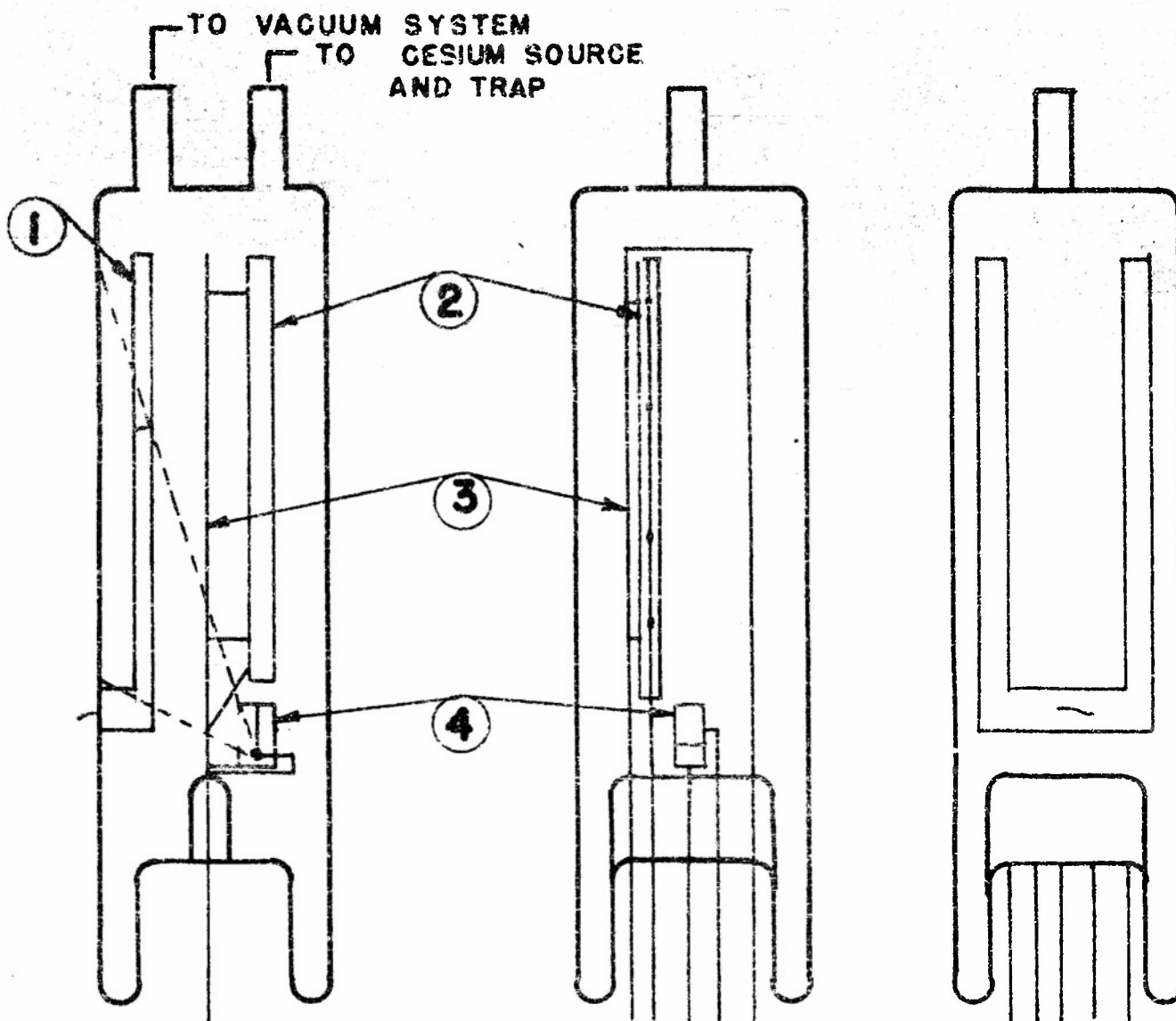
1. Lightly etch Ag cathode with nitric acid, rinse with distilled water, dry at  $1300^\circ\text{C}$ .
2. Assemble tube and seal to vacuum system.

3. Oxidize cathode with dc glow discharge in oxygen at  $\approx 0.7$  mm Hg to establish conditions for uniform oxidation. If oxidation is non-uniform, oxidize extensively, decompose oxide by heating in high vacuum at  $400^\circ\text{C}$  and re-oxidize. Repeat until uniform oxidation is obtained.
4. Degas tube at  $400^\circ\text{C}$  for several hours. Final pressure less than  $1 \times 10^{-6}$  mm Hg.
5. Oxidize surface in high voltage glow discharge to give the desired amount of deposited oxygen.
6. Evacuate tube to less than  $1 \times 10^{-5}$  mm Hg. Actual final pressure usually  $\sim 1 \times 10^{-6}$ .
7. Fire  $\text{Cs}_2\text{CrO}_4$ -Si pellet mounted in side tube.
8. Seal tube off vacuum system.
9. Mount tube in oven door bracket and attach leads from vibrating reed amplifier unit.
10. Close oven door, start timer and recorder.
11. Measure thermionic emission continuously and photo-emission periodically. Periodically determine emission current as a function of voltage. (See Section 3.1 for results.)

### 2.32 Semitransparent cathodes

Semitransparent cathodes of two types have been studied. Cathodes of the first type are prepared on bases consisting of silver films of graded thickness (wedges). Cathodes of the second type are prepared on bases consisting of silver films of uniform thickness. Evaporation of silver is continued, for cathodes of the second type, until the white light transmission is reduced to 50%. The wedge type cathodes were oxidized using a dc glow discharge, as described in Part I of this report series, to such a degree that the portion of the wedge having 50% transmission initially had 90% transmission after oxidation. Cathodes of the second type were studied chiefly in the early stages of the project and oxidations were performed using a radio frequency (rf) glow discharge. Transmission after oxidation was usually less than 90% since, as explained in Part I, transmission passes through a maximum as oxidation proceeds and the rf discharge oxidizes so rapidly that the maximum is passed before its presence is even suspected. Tube designs and preparation methods are given below for cathodes of these two types.

To study the effect of the silver film base thickness the tube design shown in Fig. 11 was developed. In this tube a silver film of graded thickness (wedge) can be evapo-



**LEGEND**

- 1. SILVER CATHODE CONTACT STRIP
- 2. SILVER BEAD LINEAR EVAPORATOR
- 3. GLOW DISCHARGE ANODE
- 4. SILVER WEDGE EVAPORATOR

**FIG.-II WEDGE PHOTOTUBE**



rated and it is also possible from the "linear" evaporator to deposit additional silver layers which approximate to a uniform thickness. The contact strip (1 of Fig. 11) is formed by evaporating a gold film in the form of a U which makes contact to the outside by means of a tungsten wire sealed through the glass envelope.

The fabrication procedure for tubes PT31W and PT32W, which are of the wedge type, is as follows:

PT31W (see Section 3.52 for results)

1. Assemble tube and seal to vacuum system.
2. Degas at 390°C, 1.5 hours. Final pressure =  $2 \times 10^{-7}$  mm Hg.
3. Evaporate silver wedge to give 50% transmission at 2.0 cm down from top of gold strip. Evaporation time 1 minute.
4. Oxidize 50% transmission silver to maximum transmission, 83% T.
5. Evacuate.
6. Fire Cs pellet in side tube using induction heating.
7. Heat tube to 180°C (18 minutes) using hot air oven.
8. Distill in cesium from trap using auxiliary furnace. Pass maximum thermionic emission and introduce some excess cesium into the tube. Bake tube 4 minutes after cooling cesium source.
9. Seal phototube off from vacuum system and measure spectral response using standard conditions. Cesium trap cooled with dry ice-acetone mixture.
10. Bake No. 1 at 160°C for 1 hour. Trap cold.
11. Measure spectral response. Trap cold.
12. Bake No. 2 at 140°C for 1 hour. Trap cold.
13. Measure spectral response. Trap cold.
14. Bake No. 3 at 130°C for 10 minutes, add cesium. (Entire tube heated).
15. Measure spectral response.
16. Bake No. 4 at 130°C for 15 minutes. Cesium addition. (Entire tube heated).
17. Measure spectral response.
18. Bake No. 5 at 160°C for 78 minutes. Trap cold.
19. Measure spectral response.

PT32W (see Section 3.52 for results)

1. Degas at 350°C to  $2 \times 10^{-7}$  mm Hg.
2. Evaporate Ag wedge to give 83% T at 1.3 cm from gold strip tip. Add Ag from "linear" evaporator to give 50% T at 1.3 cm. (Ag bead in wedge evaporator too small).
3. Oxidize 50% transmission region beyond peak transmission to give 64% final transmission using dc glow discharge.
4. Evacuate tube.

5. Fire  $\text{Cs}_2\text{CrO}_4$ -Si pellet in side tube.
6. Heat tube to  $180^\circ\text{C}$  for 17 minutes.
7. Distill in cesium from side tube at  $130^\circ\text{C}$ . Pass maximum thermionic emission and introduce slight cesium excess. Cool Cs source and bake tube 3 minutes.
8. Cool tube and tip off from vacuum system.
9. Measure spectral response. Trap cold.
10. Bake No. 1 at  $125^\circ\text{C}$ , 25 minutes, measure final response. Trap cooled.
11. Bake No. 2 at  $125^\circ\text{C}$ , 25 minutes. Measure final spectral response. Trap cold.
12. Evaporate Ag from "linear" evaporator past peak photo-emission. Measure response. Trap cold.
13. Bake No. 3 at  $125^\circ\text{C}$ , 75 minutes. Trap cold. Measure spectral response.
14. Bake No. 4 at  $152^\circ\text{C}$ , 200 minutes. Trap cold but at room temperature several hours prior to spectral response measurement.
15. Redetermine response 48 hours later with trap at room temperature during entire time.

The semitransparent 50% transmission silver film tubes which have been prepared differ from the wedge tubes described above in the following manner. The silver evaporator unit consisted of a sample head silver source mounted in an evaporator unit similar to that for the wedges and located directly opposite the central cathode area. Contact with the tungsten lead-in wire was made by the overlapping of the evaporated silver film onto a chemically deposited platinum ring contact surface formed on the glass surface. The cesium addition was performed by either (1) heating a tantalum channel containing  $\text{Cs}_2\text{CrO}_4$ -Si and mounted within the tube or (2) heating a side tube cesium source similar to that used in the massive cathode tubes. In the case of the semitransparent cathodes prepared during the early phases of the photosurface studies it was not recognized that a maximum existed in the percent transmission versus oxidation time curve. Consequently for the surfaces of this type discussed in the following chapter the silver was, for all practical purposes, completely oxidized.

The general procedure for the preparation of the semitransparent 50% transmission cathodes (see Section 3.31) is as follows:

1. Assemble tube and seal to vacuum system.
2. Degas several hours at  $375 - 400^\circ\text{C}$ .
3. Evaporate silver film to 50% transmission.

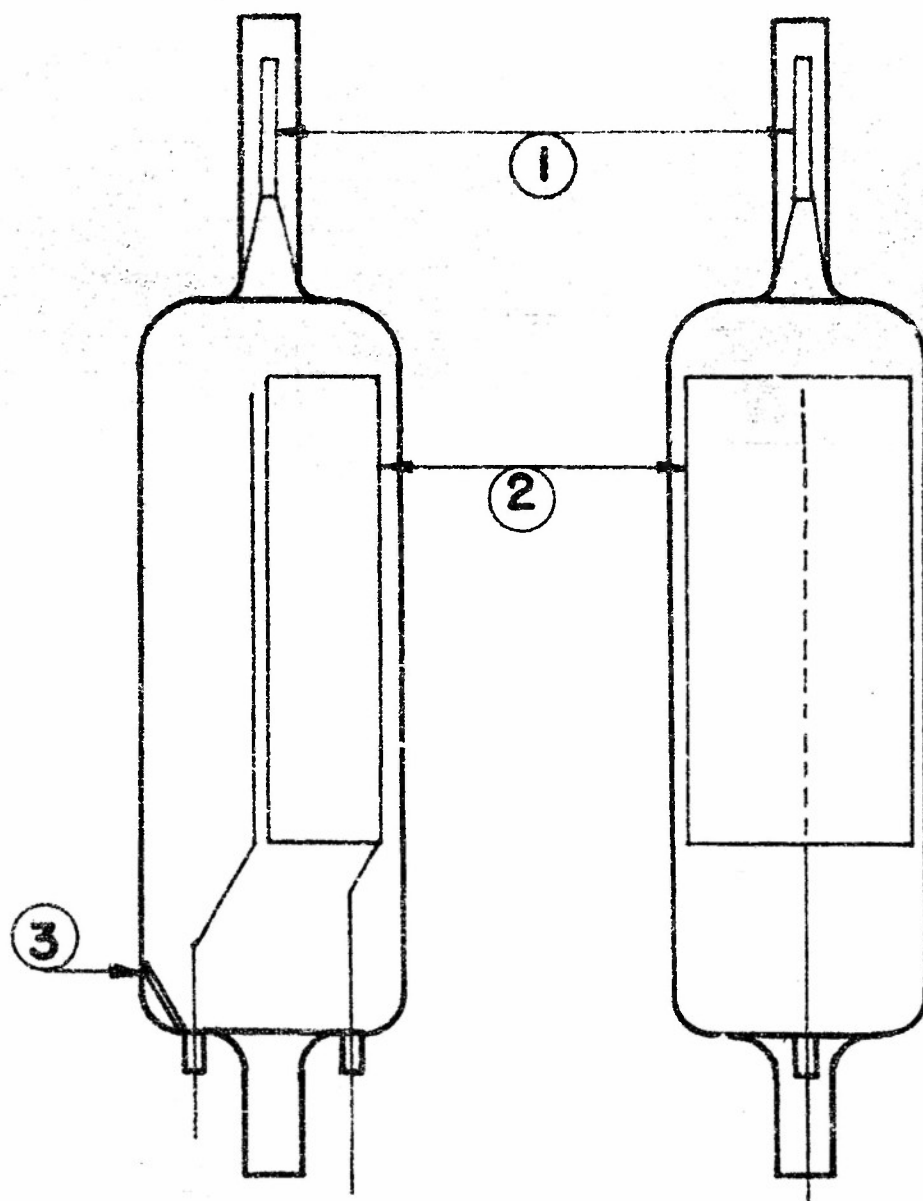
4. Oxidize to maximum transmission using rf or high voltage glow discharge.
5. Evaporate second silver layer to give 50% transmission.
6. Heat tube to 180 - 190°C.
7. Add cesium to maximum thermionic emission.
8. Cool cesium source to produce second maximum thermionic emission.
9. Cool tube and tip off from vacuum system.
10. Bake at 130°C for 3 hours.
11. Evaporate silver to maximum white light photoemission.
12. Bake at 130°C.
13. Determine spectral response.

### 2.33 X-ray diffraction phase identification cathodes

To determine the chemical species responsible for the infrared sensitivity of the Ag-O-Cs cathode a series of massive cathode tubes were prepared which permitted the x-ray diffraction determination of the phases present.

The design of the x-ray phase identification tube is shown in Fig. 12. The desired photosurface is prepared on the massive silver cathode using the technique described in Section 2.31. After determining the spectral response of the finished cathode, a sample of the photosurface is removed by scraping with a razor blade which is mounted in the tube. The razor blade is manipulated in the evacuated tube by means of a large permanent magnet. After scraping, the sample is shaken into the small capillary sealed to the end of the tube, and the spectral response remeasured to establish whether or not the photoemission changed during this operation. The top portion of the protective sleeve surrounding the capillary is then removed and an x-ray diffraction photograph of the sample in the capillary is prepared. The capillary is not removed from the tube. Thus, by remeasurement of the spectral response after the x-ray photographs are prepared, it is possible to establish whether any significant changes have occurred within the tube during the processing.

The x-ray diffraction photographs were prepared using a flat film cassette camera with a 5-cm sample to film distance in conjunction with a copper target x-ray tube. To reduce the required exposure time, unfiltered copper radiation was used. In order to definitely identify the lines resulting from the copper K $\alpha$  radiation a  $\frac{1}{2}$  inch wide nickel filter strip was placed across the central section of the film. Thus, from the variation in the intensity of the lines ap-



**FIG. 12 - MASSIVE CATHODE TUBE FOR  
X-RAY DIFFRACTION STUDY OF  
PHOTOSURFACE**

**LEGEND**

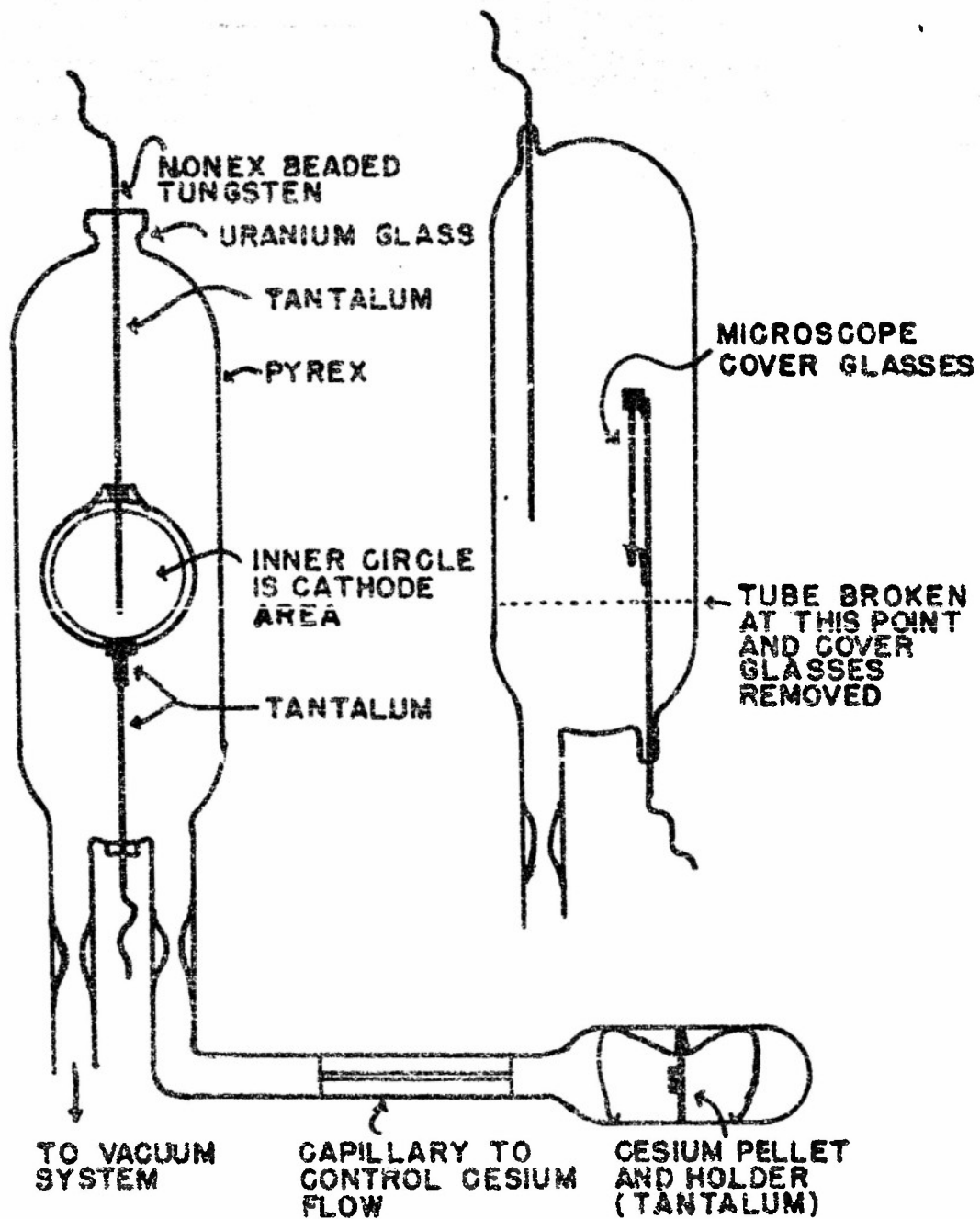
- 1. X-RAY POWDER SAMPLE CAPILLARY
- 2. SILVER CATHODE
- 3. RAZOR BLADE FOR SCRAPING CATHODE

pearing in the two regions it was readily possible to identify the lines produced by the  $K_{\alpha}$  and  $K_{\beta}$  radiation. In the preparation of the samples it was necessary to use considerable care in scraping to obtain the maximum concentration of cesium oxides relative to silver. In general, the silver lines were very intense and were used to calculate an accurate value for the film to sample distance. In the case of several tubes the razor blade was appreciably oxidized during the degassing operation. When this oxide film reacted with cesium, the iron formed did not adhere well to the blade and consequently contaminated the photosurface sample. These cathodes were not considered satisfactory for the phase identification study since the final cesium oxide concentration was too low to permit definite phase identification. This difficulty was overcome by mounting the silver sheet cathode tightly against the tube envelope with the razor blade behind it during oxidation. Oxidation of the blade was thus eliminated and satisfactory samples obtained.

#### 2.4 Tube Fabrication. Radioactive Tracer Tubes.

To determine the photosurface gross composition it was necessary to first establish that during glow discharge oxidation only a negligible fraction of the oxygen is deposited on the auxiliary tube elements. For the oxidation conditions used, it was found that tantalum did not oxidize to an appreciable extent (see Part I). To define the tube fabrication conditions it was also necessary to establish that, at 190°C, the silver oxide ( $Ag_2O$ ) decomposition rate was negligible for the period of time required to prepare the surface (see Part I). A third requirement was imposed by the problem of determining the concentration of radioactive cesium on the finished photocathode. The photocathode shape and area had to be accurately reproducible and suitable for activity measurements with a Geiger Counter.

After considerable preliminary work the final tube design shown in Fig. 14 was developed. In this tube the cathode surface consists of an evaporated silver film deposited on a 22 mm diameter microscope cover glass which is mounted in a tantalum clip cathode support. Electrical contact with the silver support is formed by a small tongue of evaporated silver which is inserted in the lower tantalum clip. During glow discharge oxidation the silver tongue was not visibly oxidized and thus the cathode area ( $2.86\text{cm}^2$ ) is well defined. To eliminate cesium deposition on the back of the



**FIG. 14-TUBE DESIGN**



cathode cover glass, a second cover glass was mounted in back to form a unit. This permitted the determination of the cesium concentration on the backing surface. The preparation of the radioactive  $\text{Cs}_2\text{CrO}_4$ -Si pellet was discussed in Section 2.2. Vacuum system II (see Fig. 22 of Part I) was used in the preparation of these cathodes.

The procedure used to prepare the silver surface proved to be important. It was found that the conditions used for evaporation, heat treatment, and oxidation could exert a profound effect upon the photoelectric and thermionic emission of the final surface. The following general procedure is used to prepare the cathode. After thorough cleaning the microscope cover glass is mounted in a stainless steel holder which accurately defines the silver cathode area ( $2.86\text{cm}^2$ ). This unit is placed in a definite position over a tantalum filament mounted in a DPI vacuum evaporator unit. After evacuation and a glow discharge bombardment, nearly spectroscopically pure silver is evaporated onto the cover glass. After mounting the combined cathode disc and the backing disc in the tantalum clip cathode support, the surface is given a preliminary oxidation in an auxiliary high vacuum system. The oxide is then decomposed by heating. This step is necessary in order to obtain uniform glow discharge oxidation and to reduce the possibility of silver sputtering in the experimental tube. The tube as finally assembled is shown in Fig. 14. The approximate area of the whole glass envelope is  $80\text{cm}^2$ .

The procedure involved in the preparation of an experimental tube is as follows: (Method D)

1. Define tube fabrication conditions: the amount of oxygen to be deposited, the final gross composition Cs/O mole ratio, and the cesium flow rate.
2. Construct capillary and cesium source unit and mount  $\text{Cs}_2\text{CrO}_4$ -Si pellet.
3. Evaporate silver on glass disc under specified conditions. (Amount of silver deposited was determined by weighing the cover glass (on a microbalance) before and after evaporation of silver layer.)
4. Assemble tube and seal to vacuum system II.  
(Note: In some of the later experiments this step was preceded by repeated oxidation and thermal decomposition in an auxiliary vacuum system to assure uniform oxidation. The oxide was completely decomposed just before step 4. This procedure serves, perhaps, in some measure to replace the nitric acid etch of methods A and B, for "roughening" the silver base.)

5. Determine volume of vacuum system with attached tube using gas expansion technique.
6. Calibrate micro Pirani gauge.
7. Oxidize cathode to determine whether or not the surface oxidizes uniformly and to aid in cleaning up the tube envelope.
8. Degas tube for approximately  $1\frac{1}{2}$  hours at approximately  $390^{\circ}\text{C}$ . This also completely decomposes the oxide formed in 7 above and leaves a clean silver surface.
9. Oxidize cathode to desired extent using dc glow discharge in oxygen.
10. Evacuate tube.
11. Degas cesium pellet and then fire it using induction heating.
12. Seal tube off vacuum system.
13. Add cesium, using the oven system of tube fabrication, to the desired extent then cool to room temperature.
14. Measure spectral response with Beckman DU spectrophotometer under standard conditions.
15. Seal off cesium source.
16. Rebake cathode.
17. Remeasure spectral response.
18. Puncture tube envelope with hot tungsten rod and crack envelope as shown in Fig. 14.
19. Remove cathode discs from tube envelope.
20. Determine concentration of cesium on the cathode surface and also on the backing disc using the procedure described in the following paragraphs.
21. Calculate photocathode Cs/O mole ratio from the measured activity and the amount of oxygen deposited during oxidation and designate this quantity by (Cs/O) count.
22. Calculate phototube Cs/O mole ratio using the capillary flow equation and the amount of oxygen deposited during oxidation and designate this quantity by (Cs/O) flow.

Prior to discussing the determination of the cesium concentration it is worthwhile to note that the tube design used is primarily determined by the problem of determining the Cs<sup>134</sup> concentration on the finished cathode surface. A suitable semitransparent cathode tube in which the cathode geometry is fixed and reproducible and the silver oxide distribution is uniquely defined is difficult to prepare.

The cesium determination involves the comparison of the cathode activity to the activity of a set of standard samples. The actual counting of the cathodes, the backing disc, and standards, is performed using the Geiger-Muller tube-sample geometry shown in Fig. 13. The active glass disc is mounted in a recess in a brass plate. Since the brass

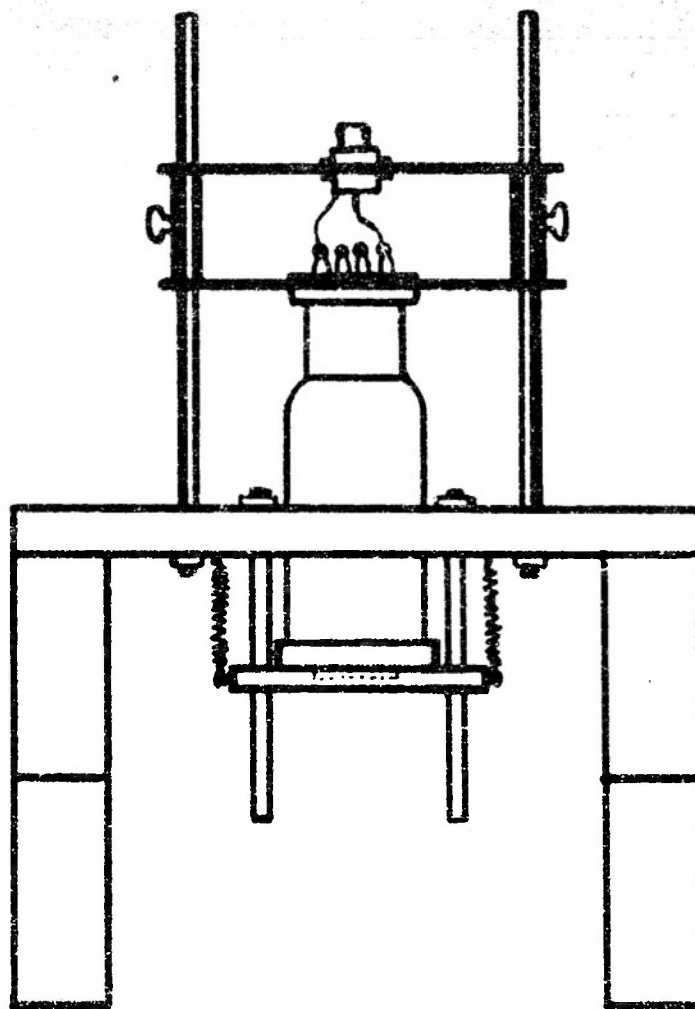


FIG.13 -COUNTING GEOMETRY

plate is tightly pressed against the Geiger tube, the cathode is very close to the mica counter window. Moreover, in different experiments the positioning of the cathode could be accurately reproduced. A nucleometer scaler was used to measure the counting rate.

The standard discs used to relate the cathode activity to actual cesium concentration are prepared in the following manner. Silver films are evaporated onto several cover glasses and partially oxidized in the auxiliary vacuum system. The oxidation of the surface provides a substrate on which a drop of solution tends to spread rather uniformly over the surface. During the radioactive pellet preparation a 0.025 ml standard sample is removed from the solution containing a known concentration of added  $\text{CsCl}$  and is deposited on the surface of the oxidized silver described above. Several standard samples are prepared in this manner for every batch of tracer  $\text{Cs}_2\text{CrO}_4$  prepared. The standards, having an activity of approximately 5,000 counts per minute, are measured each time a cathode is counted to eliminate possible errors associated with the reproducibility of the Geiger-Muller counter-tube. This rather elaborate process for preparation of standards is used in order that the environment of radioactive cesium in the standards be as nearly as possible like that in an actual cathode. Thus the radioactive samples are distributed in the same way with respect to the Geiger tube and counting errors minimized. At the same time the stopping power of the cathodes for  $\beta$  particles must be closely similar to that for the standards although the thinness of the oxidized layer probably makes the error due to the latter factor small in any case. Thickness of the oxidized layer ( $\sim 2000\text{\AA}$  at most) is small in comparison to the mica window of the counter tube (2% at most).

In counting the cathode and standards sufficiently long counting times are used to assure an accuracy of 1% in the number of counts. The cathode backing disc activity is normally measured for a period of time corresponding to a probable error of 10%. After correcting the observed counts for the background and counter dead time the cesium concentration is calculated.

The above procedure can best be illustrated by means of an example. The cesium chloride solution for pellet batch #1 was made up by adding 19.936 ml of tracer solution to 0.1815 grams of non-radioactive  $\text{CsCl}$  to form a solution containing 7.183 mg cesium per ml. (The amount of cesium in the tracer is negligible compared to the amount of non-radioactive cesium in  $\text{CsCl}$ ). Since 0.025 ml are placed on each

standard it follows that each standard contains 0.180 mg Cs. We now consider the experimental data on phototube 659-33. The cathode activity was 15,265±58 counts/min. While the activity of the standard measured simultaneously was 4293±246 counts per minute the background being 62 c/m. The deviation shown for the standard is the average deviation of the counting rates for five discs from the mean. In order to correct for counter dead time we use the formula

$$R = \frac{R^1}{1 - R^1 t}$$

where  $R^1$  is the observed count,  $t$  is the counter dead time (200 micro sec) and  $R$  is the corrected count. Thus we find for the corrected counting rates (subtracting background) cathode 16,009 c/m, standard 4,278 c/m. The counting rate per mg cesium is  $4278/.180 = 23,766$ , and hence the cathode contains 0.6736 mg Cs or  $5.072 \times 10^{-6}$  gm atoms Cs.

The uncorrected counting data for all the tubes containing radioactive cesium are given in Table VI. The preparation of these tubes and the significance of the data are fully discussed in Section 4. We wish here to call attention to the behavior of the standards. Tubes from 659-42 to 1588-165 inclusive were made up from the same batch of  $\text{Si-Cs}_2\text{CrO}_4$  pellets. The same standards were used in all of these cases and hence the counting rates for standards of this series given in Table VI represent re-counts on the same set of discs. In the 105 days which elapsed between the preparation of 659-42 and 1588-165 the counting rate of the standards decreased by about twice as much as would be anticipated from the reported half life of  $\text{Cs}^{134}$ . This might be due to an error in the reported half life. It is more probably due, however, to some systematic change in measuring technique such e.g. as the Geiger tube. It is for precisely this reason that standards are re-counted at the same time as a cathode activity is measured. In all cases the amount of cesium in a cathode is calculated by comparison of cathode activity to the activity of the standard measured at the same time. Thus systematic changes in the Geiger tube are corrected for. There is another possibility, however, which must be mentioned. It is possible, although unlikely, that the counting rates for the standards decreased more rapidly than expected because of loss of active material. The question is raised not because of the behavior of standards but because of the behavior of the cathodes. It was found that cathodes which had been standing in the laboratory (after removal from the

TABLE VI. RADIOACTIVE PHOTOCATHODES

Tube No.	Standards	Counts per Minute		
		Cathode	Backing Disc	Background
659-16	4653±69(4)	1269±22	450±9	59
659-19	4533±23(3)	1924±1	183±1	57
659-28	4771±43(3)	1064±2	370±12	67
659-33	4293±246(5)	15265±58	350±2	62
659-42	8135±76(4)	2486±20	500±1	63
659-46	8442±70(4)	1812±9	293±5	90
1588-111	8441±178(4)	2128±22	159±2	86
1588-122	7644±37(4)	4489±16	171±2	86
1588-130	7681±157(3)	6754±44	303±7	80
1588-137	7820±78(3)	5054±25	187±10	87
1588-145	7574±40(3)	2080±25	382±12	96
1588-165	6960±87(2)	1538±96	164±4	86
1588-180	7506±129(6)	15000±35	237±7	79
1588-186	7563±119(6)	9122±65	286±2	71
1588-192	7429±121(6)	5415±31	122±4	81
1588-198	7305±116(6)	8277±3	202	74
1588-200	7300±135(6)	4627±20	179	68

1. Pellet batch #1: Each standard contains 0.180 mg. cesium.
2. Pellet batch #2: Each standard contains 0.471 mg. cesium.
3. Pellet batch #3: Each standard contains 0.320 mg. cesium.

Note: The deviations given for the standards are mean deviations of the average counting rates for the various discs from the average of all discs. These deviations therefore give a measure of the scatter among various discs. The remaining deviations arise as the result of several measurements on the same sample and hence indicate the deviation in counting rate measurement.



phototube) tended to lose activity much more rapidly than the standards. This behavior was finally traced to the transfer of active material from the cathodes to the surrounding containers in which they were stored. We can only attribute this to the fact that cesium oxides in the cathode are gradually converted to cesium hydroxide in air and the latter substance is deliquescent. On absorbing moisture crystal fracture and spattering occurs which distributes material through the surroundings. This is less likely with the standards since they contain  $\text{CsCl}$  which is not deliquescent. Moreover, very little activity could be detected in the surroundings in this case so the error introduced is probably small. Even if we attribute the whole difference between the measured activity of the standards and that computed from the half life to loss of active material it would amount to only about 6% and we are inclined to think that the actual error from this source is very much less than this maximum estimate especially since there is no reason to think that a Geiger tube gives reproducible results over an extended period of time. One final point must be noted. In the second column of Table VI the number in parentheses gives the number of standard discs counted. It will be noted that for tubes 1588-130, 137, and 145, only three were counted and for 1588-165 only two. This arises because one disc and then another departed so widely from a regular trend that the results were considered unreliable and were omitted from the average. These changes took place abruptly and rather strongly suggest that some active material was accidentally removed from these two standard discs, perhaps in handling. If all standard discs had been included in the average the counting rates for the 1588-130, 137, and 145, standards would decrease by less than 5% below the figures given in the table. In the case of tube 1588-165, however, a decrease of 10% would occur. It is believed that the results included in the table are correct but there is an element of judgement involved in the case of the four tubes mentioned which is significant in the case of 1588-165. In the remaining cases no question arises. It will be evident from the discussion of Section 4 that even the largest of the above errors does not influence the interpretation of the data.

It is of interest to have some estimate of error involved in the determinations. Taking into account all factors including errors in pressure measurement, loss of oxygen on heating, errors in counting rate measurement etc. we have estimated 15% as the maximum error in a single observation of the  $(\text{Cs}/\text{O})$  ratio and the probable error as



about 3%. The results of these experiments are discussed in detail in Section 4.

It must finally be noted that the loss in activity of the cathodes mentioned above has no influence on the accuracy of measurement. For the change in activity was measured after the cathode had been removed from the phototube envelope and was exposed to air. If a graph is constructed of loss in activity as a function of time and a straight line drawn through the somewhat scattered points then the slope of the line indicates a loss of about 1% per day. The cathode count, used in the composition measurement, was, however, taken not more than twenty minutes after fracturing the phototube envelope and hence the loss in activity is negligible.

### 3. PHOTOELECTRIC AND THERMIONIC EMISSION

- 3.1 Development of Thermionic and Photoelectric Emission
  - 3.11 Continuous Cesium Addition
  - 3.12 Interrupted Cesium Addition
  - 3.13 Effect of Temperature on Photoelectric Emission
  - 3.14 Photoactivation of Thermionic Emission
  - 3.15 Effect of Voltage on Photoelectric and Thermionic Emission
  - 3.16 Oxide Layer Thickness
  - 3.17 Tube Geometry
  - 3.18 Definition of a "Normal Tube"
- 3.2 "Commercial" Fabrication of Massive Cathode Phototube
  - 3.21 Tube Fabrication
  - 3.22 Spectral Response Characteristics
  - 3.23 Long Wavelength Spectral Yield
  - 3.24 Development of Infrared Response
  - 3.25 Discussion
- 3.3 Distillation Technique for Preparation of Photocathodes Containing Cs<sub>2</sub>O
  - 3.31 Semitransparent Photocathodes
  - 3.32 Massive Cathodes
- 3.4 Baking and Excess Cesium
  - 3.41 Cesium Addition at Room Temperature
  - 3.42 Baking and Infrared Sensitivity
- 3.5 Effect of Silver Base on Photoelectric Emission
  - 3.51 Thick Evaporated Silver Films
  - 3.52 Evaporated Silver Wedge Cathodes
- 3.6 Photocathode Stability
- 3.7 Discussion

### 3. PHOTOELECTRIC AND THERMIONIC EMISSION

It has previously been pointed out several times that the Ag-O-Cs photocathode is difficult to prepare reproducibly. On account of this variability it was necessary to conduct a good deal of essentially exploratory work so as to establish the most suitable conditions for cathode preparation in our own work. Much of this work is described in the present section and is organized in such a way as to indicate the effect of various process variables which have been studied. Along with this work experiments have been conducted in which the photoelectric and thermionic emission are continuously followed as cesium is slowly added to an oxidized silver cathode (see Section 3.1). These Experiments showed immediately that the cathode reactions are slow. This fact and others inferred from the experiments on slow cesium addition have been very useful in interpreting the observations made during the course of the exploratory experiments described above. For this reason these experiments are discussed first, in Section 3.1.

#### 3.1 Development of Thermionic and Photoelectric Emission

The development of photoelectric and thermionic emission during the formation of a photosurface has been extensively studied. In this investigation, to avoid complications associated with the structure of thin silver films, a series of massive silver cathodes were prepared at 150° and 190°C using the apparatus described in Section 2.12. Since the products of oxidation of silver sheet under controlled conditions are relatively reproducible we are able to study the effect of various variables on the reaction between cesium and silver oxide. Thus the effect of varying the ratio of the number of cesium atoms to the number of oxygen atoms can be studied without the introduction of extraneous factors connected with the silver base.

To make the results accurately comparable the same cathode and capillary were used to prepare several tubes. This was possible because, after the preparation of one cathode, the oxides could be removed by rinsing the tube with dilute nitric acid. This did not introduce any additional contamination since, in any case, it is the practice to roughen the silver surface by means of etching.

with nitric acid. This is followed of course, by thoroughly rinsing with distilled water and drying. It might seem at first sight, as it seemed to us, that the study of some variable, such as thermionic emission, as a function of cesium content would clearly indicate the appearance of a new solid phase. For the appearance of a new phase would be attended by an abrupt change in slope of a curve of thermionic emission as a function of amount of cesium. Since the phase equilibrium diagram is known (see Fig. 1) this would locate the point at which a phase boundary is crossed. This program does not work out well in practice because the cathode reactions take place slowly. It is nevertheless useful to consider the solid phases expected (at equilibrium) at each (Cs/O) mole ratio since this provides a prediction which can be compared with the experiment. We consider the two temperatures, 150°C and 190°C, at which photocathodes are commonly prepared.

According to the phase diagram, the addition of cesium to oxygen (from oxidized silver) at 190°C results in the formation of the following species if equilibrium is established:

Composition	Phase
1. $0 < (\text{Cs/O}) < 0.5$	$\text{Cs}_2\text{O}_2(\text{s})$
2. $0.5 < (\text{Cs/O}) < 0.66$	$\text{Cs}_2\text{O}_2(\text{s}) + \text{Cs}_2\text{O}_3(\text{s})$
3a. $0.66 < (\text{Cs/O}) < 1.00$	$\text{Cs}_2\text{O}_3(\text{s}) + \text{Cs}_2\text{O}_2(\text{s})$
b. $1.00 < (\text{Cs/O}) < 2.00$	$\text{Cs}_2\text{O}_2(\text{s}) + \text{Cs}_2\text{O}(\text{s})$
or 4. $0.66 < (\text{Cs/O}) < 2.00$	$\text{Cs}_2\text{O}_3(\text{s}) + \text{Cs}_2\text{O}(\text{s})$
5. $2.00 < (\text{Cs/O}) < 2.91$	$\text{Cs}_2\text{O}(\text{s}) + \text{Cs}(\text{l})$ containing dissolved oxygen.

Thus at 190°C solid cesium oxide phases richer in cesium than  $\text{Cs}_2\text{O}$  may not be formed. The sequence of step 3 or 4 is in doubt since at the time of writing it had not been unequivocally established whether the oxide phase  $\text{Cs}_2\text{O}_2$  may be formed by direct reactions, i.e. whether it could be a possible metastable phase. At 150°C the following additional phases must be added to the sequence

- |                                 |  |
|---------------------------------|--|
| 6. $2.0 < (\text{Cs/O}) < 3.0$  | $\text{Cs}_2\text{O}(\text{s}) + \text{Cs}_3\text{O}(\text{s})$                    |
| 7. $3.0 < (\text{Cs/O}) < 3.29$ | $\text{Cs}_3\text{O}(\text{s}) + \text{Cs}(\text{l})$ containing dissolved oxygen. |

Sayama has reported that equally good photosurfaces may be formed in the composition range  $2.0\text{Cs}/0.3\text{O}$ . Consequently it is of interest to establish whether or not the phase  $\text{Cs}_2\text{O}$  is in reality a good infrared photoemitter. In addition it is of interest to establish the effect of the very slow decomposition of silver oxide at  $190^\circ\text{C}$  on the emission characteristics. At  $150^\circ\text{C}$  the rate of decomposition would be negligible.

### 3.11 Continuous cesium addition

To investigate the development of photoelectric and thermionic emission during continuous cesium addition two tubes, PT44 and PT46 were prepared at  $190^\circ\text{C}$ , and tube PT52 at  $150^\circ\text{C}$ . During the oxidation step, 13 microgram atoms of oxygen were deposited on the cathode of PT44 and 13.5 on PT46, while 9.8 microgram atoms were deposited in PT52. These amounts are sufficient for oxidation of the cathodes to the second order yellow color. The corresponding molecular flow equation cesium flow rates are as follows: PT44 -  $15.1 \times 10^{-8}$ , PT46 -  $7.2 \times 10^{-8}$ , and PT52 -  $9.84 \times 10^{-8}$  moles/min. It is to be noted that the cesium flow rate for PT46 is approximately half the rate for PT44 and corresponds to the deposition at  $190^\circ\text{C}$  of a cesium monolayer on the cathode every 0.1 minutes.

The tube PT44 was the first cathode prepared using the oven system of fabrication (see Section 2.12) to study the development of thermionic emission during cesium addition. The thermionic emission as a function of time is shown in Fig. 15. The character of the tube current, conduction or thermionic, was established by determining the variation of current with the applied voltage. During the first 80 minutes and beyond 200 minutes the current was proportioned to voltage and thus was an ohmic conduction current arising from a conducting film on the tube envelope. In the region between 90 and 190 minutes the voltage-current relationship exhibited a saturation effect typical of thermionic emission. In Fig. 15 the points corresponding to  $\text{Cs}_2\text{O}_2$  and  $\text{Cs}_2\text{O}$  gross composition were computed using the intermediate pressure flow equation and correcting for the oven warm up time. This gives the ratio of total cesium entering the tube to total oxygen (gross composition) with an error not exceeding 5%.

The thermionic emission curve has two maxima, one at 141 minutes corresponding to  $(\text{Cs}/\text{O})=1.5$  and one at 164 minutes corresponding to  $(\text{Cs}/\text{O})=1.7$ . The rapid decrease

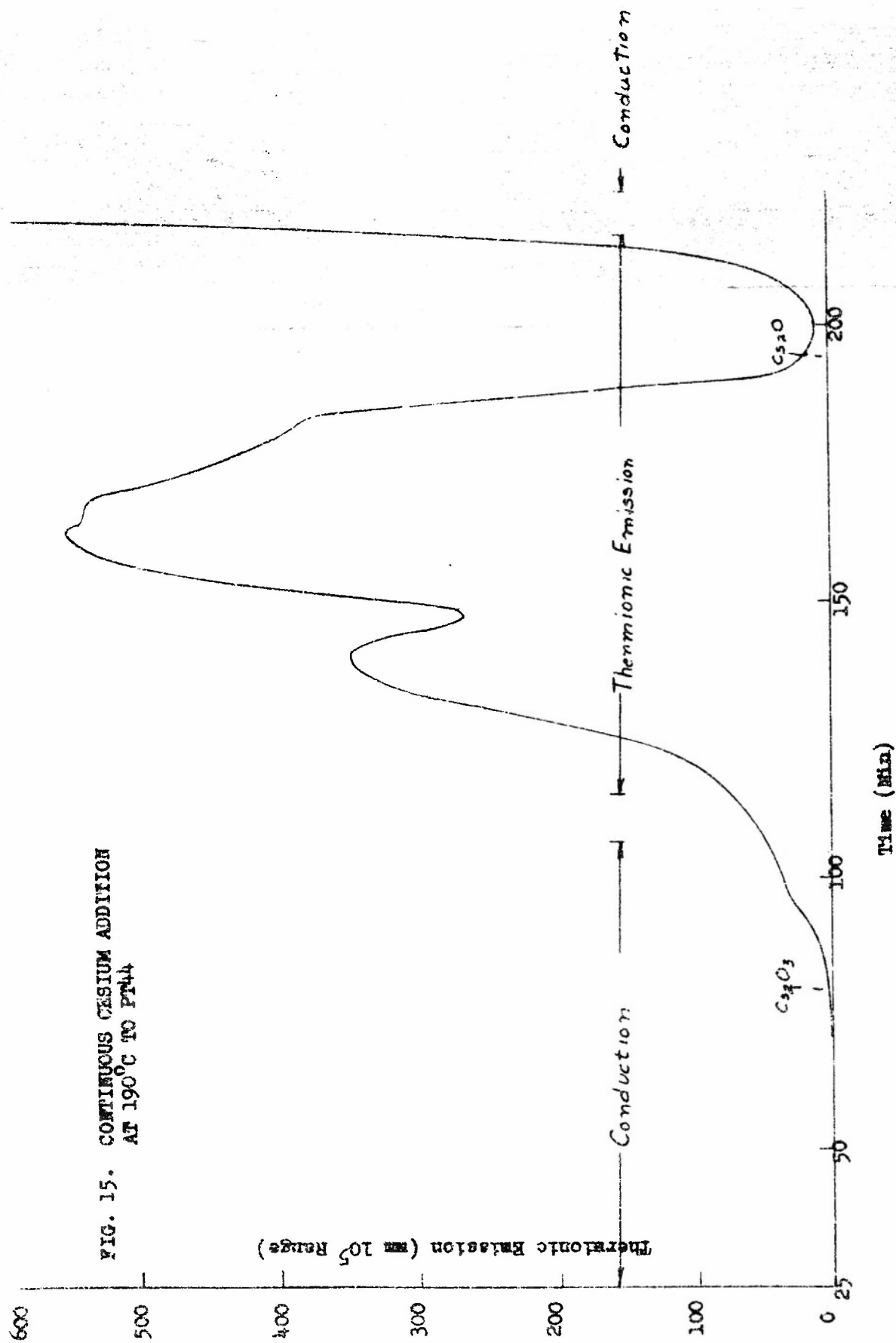


FIG. 15. CONTINUOUS CESIUM ADDITION  
AT 190°C TO Pt44

in thermionic emission between 180 and 190 minutes extrapolates to zero thermionic emission at a gross composition of nearly  $\text{Cs}_2\text{O}$ . As discussed later, the two maxima in thermionic emission arise due to the fact that not only the front but also, to some extent, the back surface of the cathode was oxidized during the glow discharge oxidation. Only one maximum is observed on cathodes with the back surfaces shielded.

The above experiment is essentially a repetition with some variation in arrangement, of the work of Campbell<sup>20</sup> and Sayama<sup>21</sup>. The results differ from those of both Campbell<sup>20</sup> and Sayama<sup>21</sup> in one important respect. Whereas they found that a maximum in thermionic emission coincides rather accurately with the composition  $(\text{Cs/O})=2$ , we do not find such coincidence. In fact both maxima of Fig. 15 occur at  $(\text{Cs/O})$  ratios significantly less than 2. The difference between this experiment and those of Campbell and Sayama is probably due to two factors: (1) the differing proportions of cesium on the tube envelopes and (2) variations from uniform cathode coverage by cesium. Reaction of cesium with the glass envelope was reported by Prescott and Kelly<sup>18</sup> and has been amply confirmed in our own work (see Section 4.1). This factor tends to make the  $(\text{Cs/O})$  ratio of Fig. 15 larger than the  $(\text{Cs/O})$  ratio for the cathode itself. It is not easy to see how the non-uniform distribution of cesium over the cathode would affect thermionic emission. If the front of the cathode received more cesium than the back, as seems probable, then the thermionic emission might reach a maximum before the back (which is somewhat oxidized) had reacted completely. This would shift the maximum to lower  $(\text{Cs/O})$  ratios. It is found, however, that even with the back of the cathode shielded the thermionic emission maximum does not come at  $(\text{Cs/O})$  ratios of 2 (see Section 4.1). It is found in general that the position of the highest maximum (see Fig. 15) can be reproduced in experiments which involve the same ratio of cathode area to tube envelope area and in which the cathode is placed in the same way with respect to the capillary inlet. When, however, the experimental photocell is drastically changed there is a change in position of the maximum (see Sections 3.17 and 4.1 for examples).

It is evident from these considerations that the  $(\text{Cs/O})$  ratios based on total cesium entering the photocell cannot be assumed equal to the  $(\text{Cs/O})$  ratios on the photocathode. The radiotracer experiments described in Section 4.1 are necessary in order to establish the  $(\text{Cs/O})$  ratio for the cathode. We shall anticipate the results of Section 4.1,



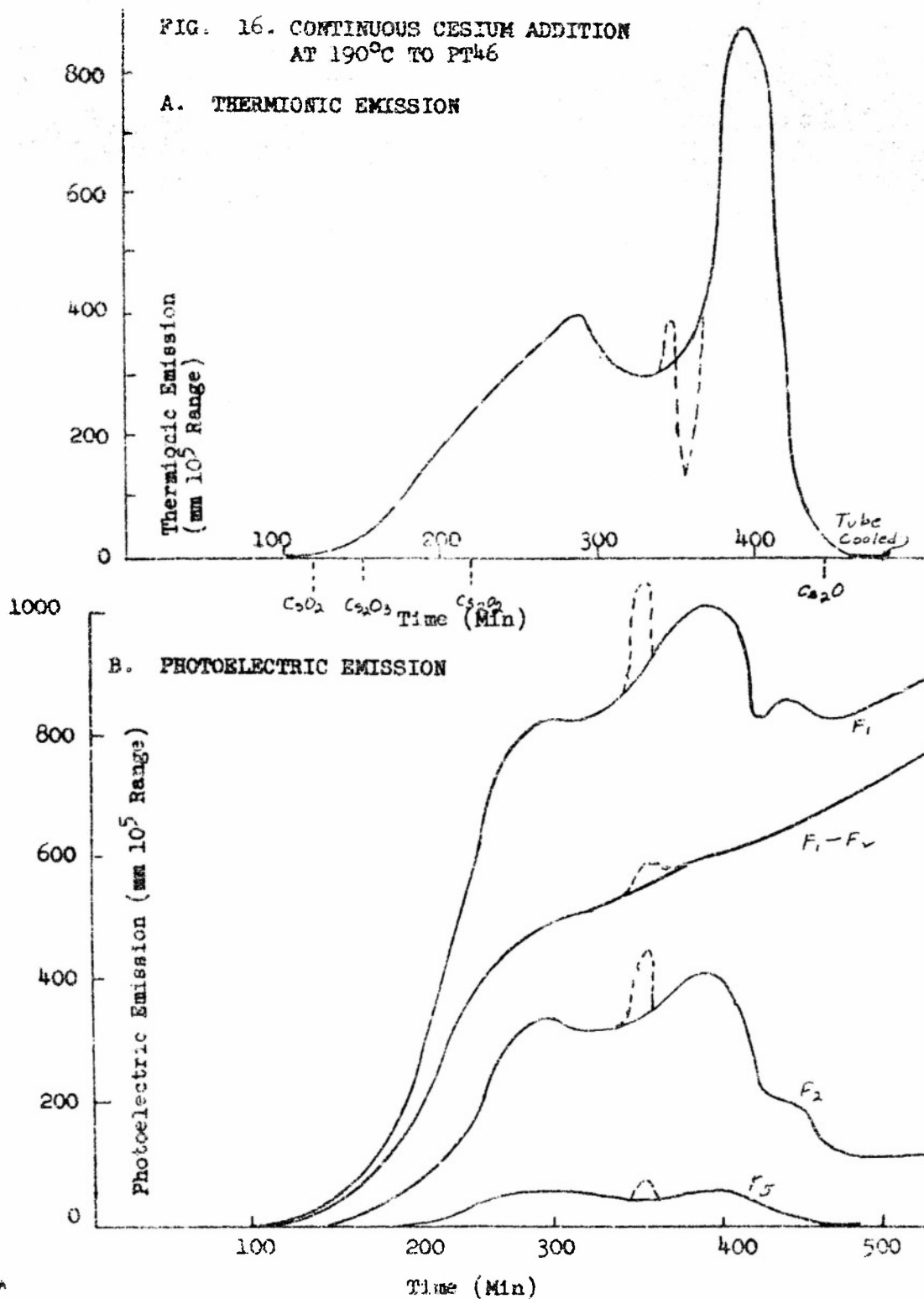
however, by remarking that the photocells of this section apparently are less affected by the two factors mentioned earlier than any others which we have studied. For the (Cs/O) ratios at maximum thermionic emission are closer to those for the cathode, presented in Section 4.1, than for cells of any other type. This remark also applies to the cells of the next section (3.12).

Inspection of Fig. 15 immediately shows that thermionic emission does not accord well with the hypothesis that chemical phase equilibrium is established in the photocathode. For if phase equilibrium were established then a sharp change in slope is to be expected when phase boundaries are crossed. This should occur at (Cs/O) ratios of 0.67 and 2 since new compounds ( $\text{Cs}_2\text{O}_3$  and  $\text{Cs}_2\text{O}$ ) would be formed at these compositions if equilibrium prevailed. This is clearly not the case. It is evident, however, that thermionic emission is somehow related to the phase equilibrium diagram. For thermionic emission exhibits a tendency to rise beyond (Cs/O)=0.67 and falls nearly to zero just beyond (Cs/O)=2. The question of phase equilibrium is again discussed below.

The development of photoelectric as well as thermionic emission during continuous cesium addition at  $190^\circ\text{C}$  was investigated with tube PT46. Since the data obtained during the preparation of PT44 suggested that with a cesium flow rate of 16 monolayers per minute the rate of reaction was slower than the rate of addition, the cesium flow rate was halved. The thermionic and photoelectric emission for PT46 as a function of time are shown in Fig. 16. The thermionic emission curve is very similar to that for PT44. The photoelectric emission, for each of the series of filters, exhibits two maxima coinciding with the appearance of the thermionic emission maxima. From the figures it is evident that the thermionic and photoelectric emissions during cesium addition do not exhibit a 1:1 correlation. The second thermionic maximum at 395 minutes is twice as high as the first maximum. The  $F_5$  infrared responses at the two peaks, however, are equal. The  $F_1$  and  $F_2$  responses at the second maximum are slightly greater than at the first maximum.

During the preparation of this cathode, the cesium source was cooled from 345 to 355 minutes by placing moistened cotton on the cesium source bulb. This reduces the vapor pressure of cesium and effectively halts the addition. The thermionic emission increased immediately to a maximum and then decreased as indicated by the dotted curve in Fig. 16A. The photo response also exhibits a marked increase as shown by the dotted curve in Fig. 16B. In fact, cooling the cesium source doubles the  $F_5$  infrared response corresponding to a very

FIG. 16. CONTINUOUS CESIUM ADDITION  
AT 190°C TO PT46



large increase in the response beyond 880 m $\mu$ . This behavior on cooling the cesium source strongly suggests that rates of the reactions at the photosurface actually are slower than the rate of cesium deposition. This is true despite the reduction in cesium flow rate to one half that for PT44.

The cesium addition was continued until the thermionic emission had decreased from 875 to 0.91 mm ( $10^3$  range). As cesium is added beyond the second maximum, the infrared sensitivity steadily decreases while the visible ( $F_1$ - $F_2$ ) response steadily increases. Cooling the cathode to room temperature results in an increase in the  $F_1$  response without significantly changing  $F_2$ . This indicates that the spectral response is increasing at wavelengths shorter than 775 m $\mu$ . It is worthwhile to note that during the cooling of the tube with a gross composition 24(Cs/O)43 the equilibrium phases formed would be  $Cs_2O(s)$  and  $Cs_3O(s)$ .

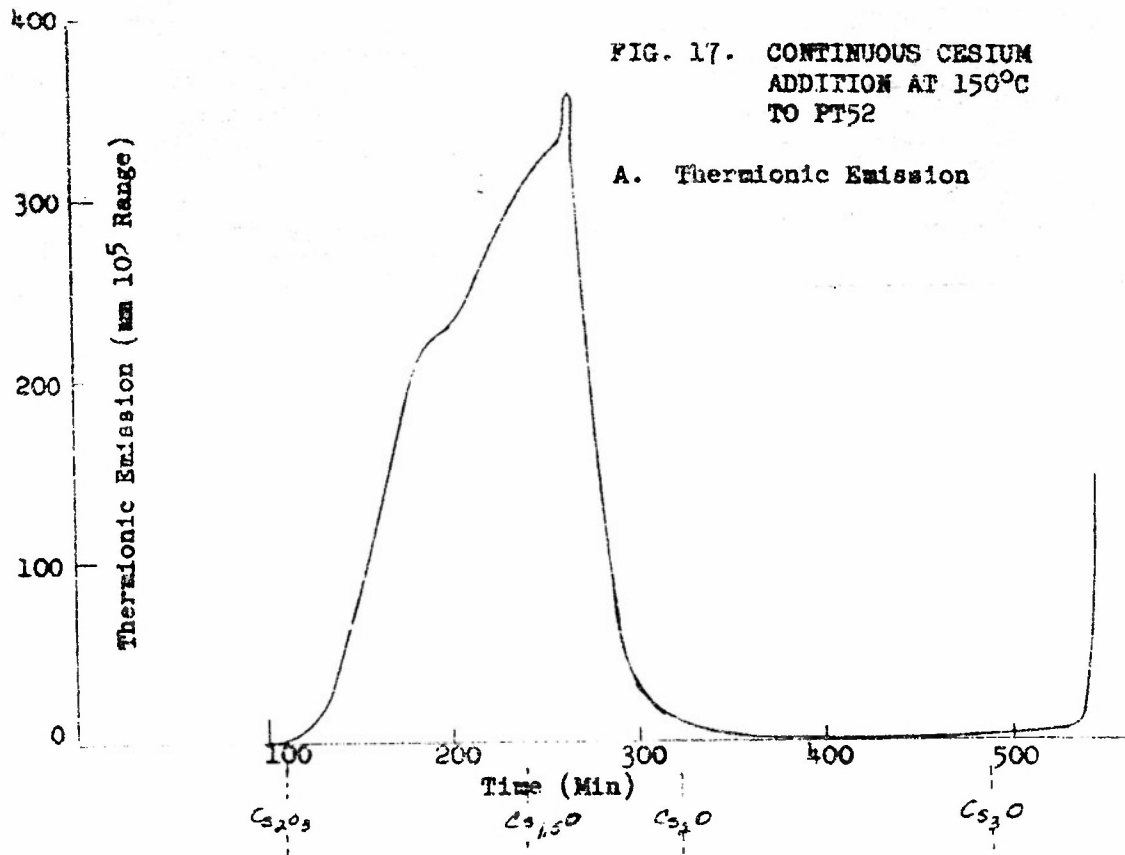
The development of photoelectric and thermionic emission during continuous cesium addition at 150°C was investigated with tube PT52. In this case the cesium addition rate is intermediate between that of PT44 and PT46. The thermionic and photoelectric emission data for PT52 are shown in Fig. 17A and B respectively. From a comparison of this figure to Fig. 16 for PT46 it is evident that the general features of the emission are quite similar in the two cases.

The maximum photoemission is obtained at the gross composition (Cs/O)=1.5 whereas the maximum thermionic emission appears at (Cs/O)=1.6. During the processing it was observed that at (Cs/O)=1.5 $\pm$ 0.2 there was a marked photoactivation of the thermionic emission which increased the thermionic emission after illumination to a value higher than if there had been no illumination. The sharp peak in thermionic emission is produced by photoactivation. The maximum emissions actually occur at approximately the same gross composition at 150° and 190°C. The absence of a marked first thermionic emission maximum at 150°C is probably related to a slight difference in tube geometry compared to the 190°C tubes.

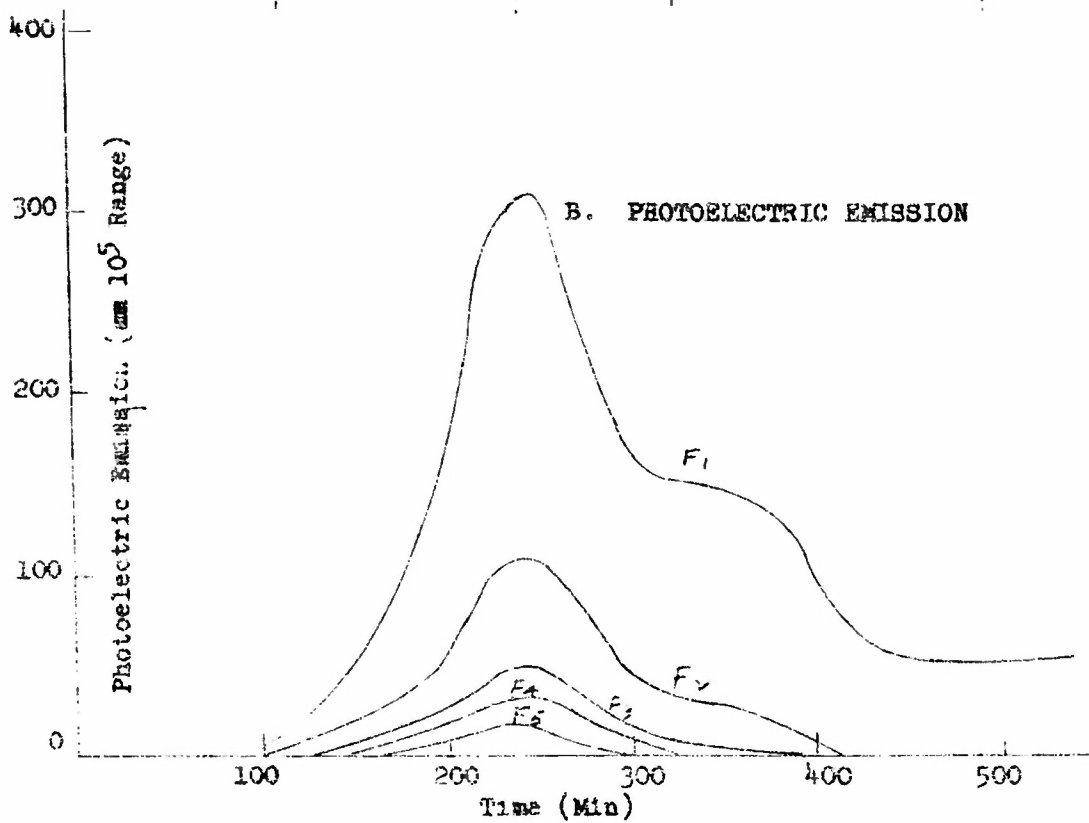
From the appearance of the photoemission curves it seems that three different types of photosurfaces are formed during continuous cesium addition. In the vicinity of maximum thermionic emission the surface having maximum infrared sensitivity is formed. As the cesium addition is continued, at 190° and 150°C, beyond maximum thermionic

FIG. 17. CONTINUOUS CESIUM  
ADDITION AT 150°C  
TO PT52

A. Thermionic Emission



B. PHOTOELECTRIC EMISSION



emission the photoemission rapidly decreases to a second state characterized by a low  $F_5$  response. At  $150^\circ\text{C}$  the resultant surface, on the basis of the filter response, is characterized by long wavelength limit greater than  $830\text{ m}\mu$  but less than  $1000\text{ m}\mu$ . Further addition of cesium at  $150^\circ\text{C}$  results in a surface without appreciable  $F_3$  response, and a very low  $F_2$  response corresponding to a long wavelength limit in the vicinity of  $800\text{ m}\mu$ . These surfaces at  $150^\circ\text{C}$  are also characterized by a very low thermionic emission. It is observed at  $150^\circ\text{C}$  that shortly before the gross composition  $\text{Cs}_3\text{O}$  is reached the emission starts to change from a thermionic emission to a conduction current. This is indicated by the fact that the tube current becomes directly proportional to the applied voltage and the reverse polarity current equals the correct polarity current. At this point, for the tube design used, the equivalent resistance is of the order of  $1 \times 10^{10}$  ohms. Cooling a cathode with only a slight excess of cesium results in a marked decrease in the conduction current, suggesting the presence of a surface semiconducting film.

Despite the fact that phase equilibrium is not exactly established it is interesting that the appearance of a conduction current can be roughly correlated with the phase equilibrium diagram. Reference to the phase equilibrium diagram shows that at  $100^\circ\text{C}$  a liquid solution of oxygen in cesium is not expected until the gross tube composition  $\text{Cs}_2\text{O}$  is exceeded, whereas at  $150^\circ\text{C}$  this solution is not expected until the composition  $\text{Cs}_3\text{O}$  is exceeded. The fact that very rapid increase in conduction current takes place soon after these compositions are exceeded (see Figs. 15 and 17A) suggests that a film of conducting liquid is forming on the tube envelope and, moreover, that the system is not too far removed from phase equilibrium.

The results indicated by Figs. 15, 16, 17 suggest that thermionic emission, and photoelectric emission, are developing as the result of something which takes place within a layer of material considerably thicker than a monolayer. The maxima in emission, indicated by the figures, occur after amounts of cesium have been deposited which correspond to several hundred monolayers. A considerable bulk of material is therefore involved. This result was indicated by the initial work of L.R. Koller<sup>19</sup> and has been confirmed by Campbell<sup>20</sup>, Sayama<sup>21</sup> and others. However, very small amounts of cesium in excess of equilibrium can markedly affect the cathode as is evident from the results of the next section.

### 3.12 Interrupted cesium addition

In order to explore more fully the suggestion that slow solid phase transformations are occurring in the photocathode several tubes have been prepared at 150°C and 190°C in which cesium flow is interrupted several times. The general characteristics of the phenomena observed are best illustrated by the data for PTL7, 190°C, and PT53, 150°C.

In the fabrication of these tubes the following oxidation and cesium flow conditions were used:

Tube	g. Atom Oxygen	Cs Flow Rate
PTL7	$1.71 \times 10^{-5}$	$7.2 \times 10^{-8}$
PT53	$0.98 \times 10^{-5}$	$6.56 \times 10^{-8}$

The flow rates listed were computed using the molecular flow equation, and thus the rates are approximately 10% high. The cathodes were oxidized to the second order colors, PTL7 to a light green and PT53 to the second order yellow. The detailed calculation of the (Cs/O) ratio as a function of time was not attempted because of the uncertainties introduced by the periodic cooling of the cesium source.

The changes in the thermionic and photoelectric emission of PTL7 when the cesium source was cooled at various processing stages are shown in Figs. 18 and 19. In the thermionic emission region before the first maximum, cooling the cesium source results in a rapid decrease in the thermionic and photoelectric emission as shown in Fig. 18A. As the first maximum is approached, cooling the cesium source results in an initial increase in both thermionic and photoelectric emission, followed by a decrease to a value less than existed before cooling. Reintroducing cesium causes the emission to increase to a second maximum followed by a decrease to the original value observed before cooling the cesium source. In PTL7 the first maximum occurred at 375 minutes. Thus the curves in Figs. 18B and C illustrate the changes in thermionic emission in the region of this first maximum. It is of interest to note that corresponding to the decrease in thermionic emission, the infrared emission decreases without marked changes in the ( $F_1-F_2$ ), i.e. visible, response. This suggests that there actually may exist two kinds of centers giving rise respectively to the visible and infrared sensitivity, the latter being related to the

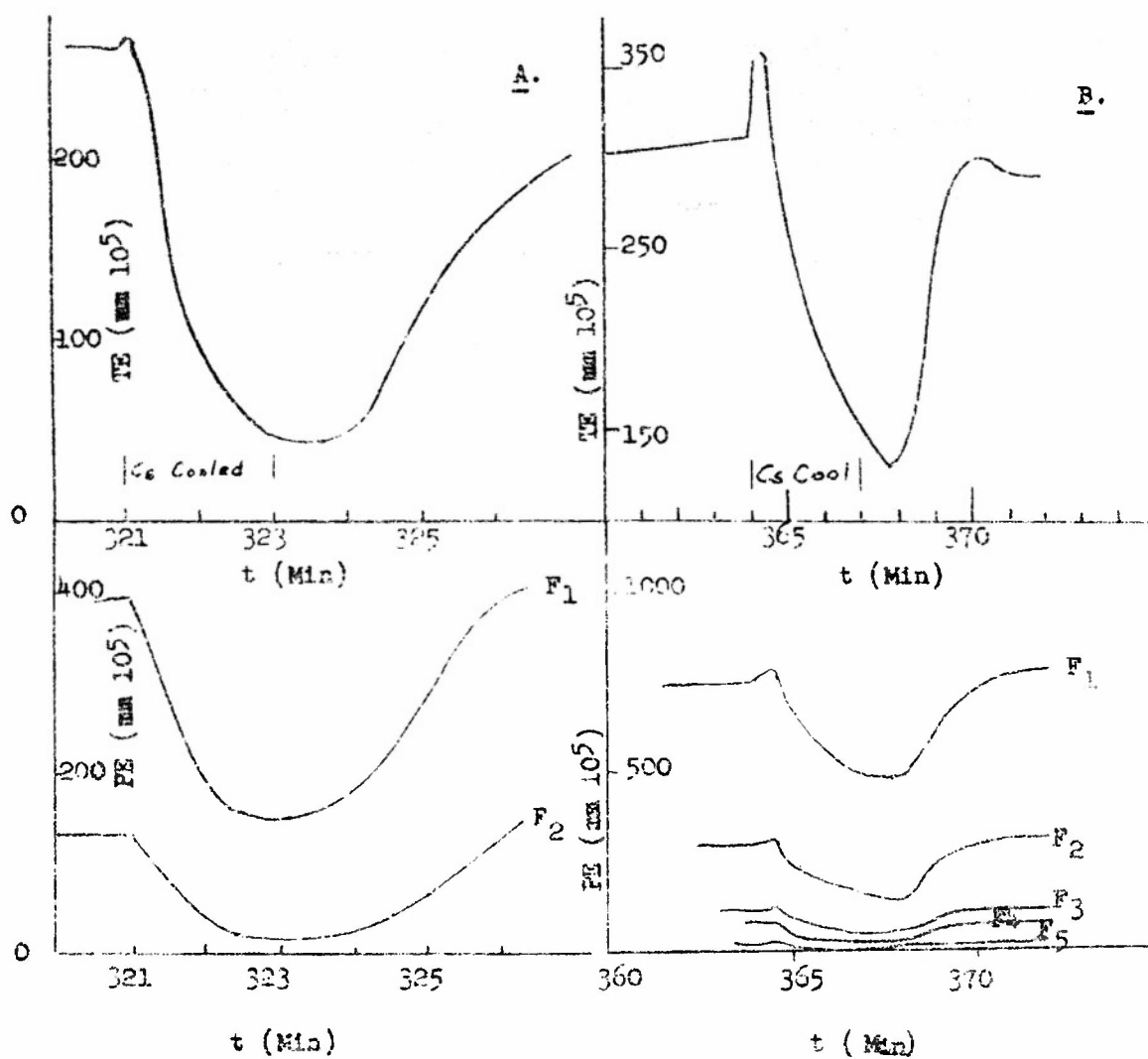


FIG. 18 A - B. EFFECT OF CESIUM SOURCE COOLING  
AT 190°C - PT47



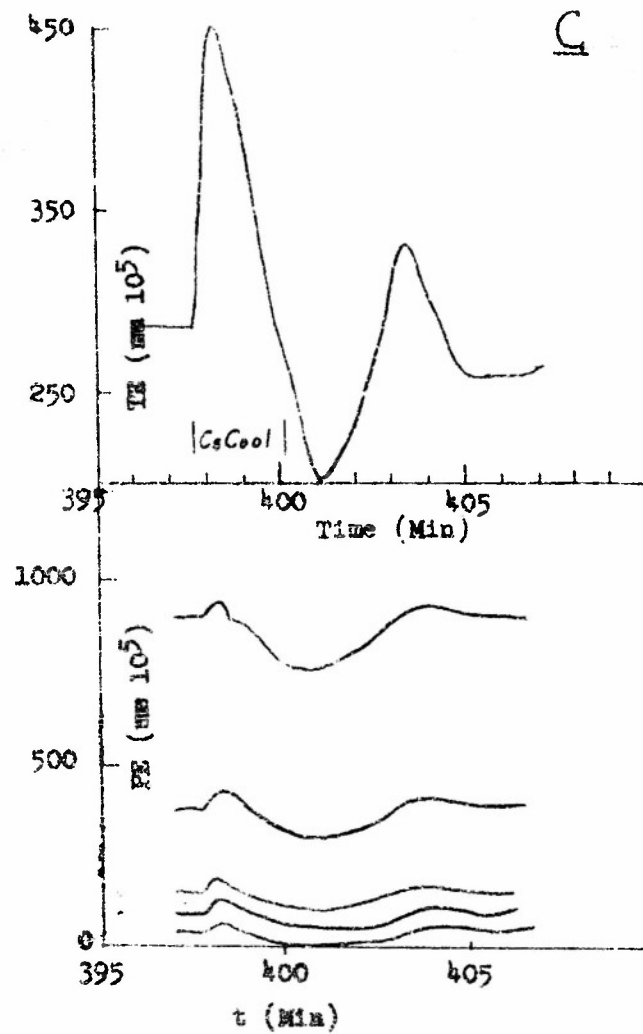


FIG. 18 C. (Continued)

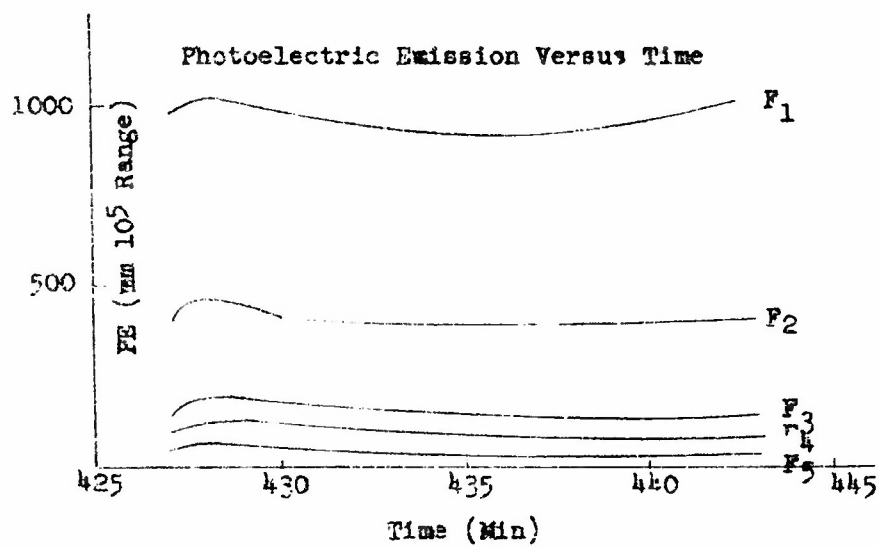
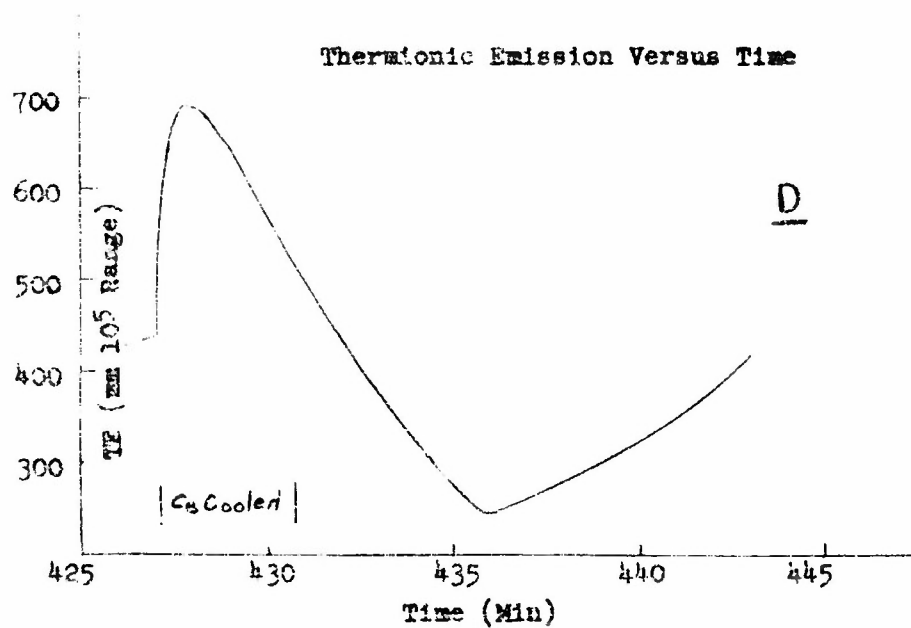


FIG. 19 D. EFFECT OF CESIUM SOURCE COOLING AT 190°C - PT47

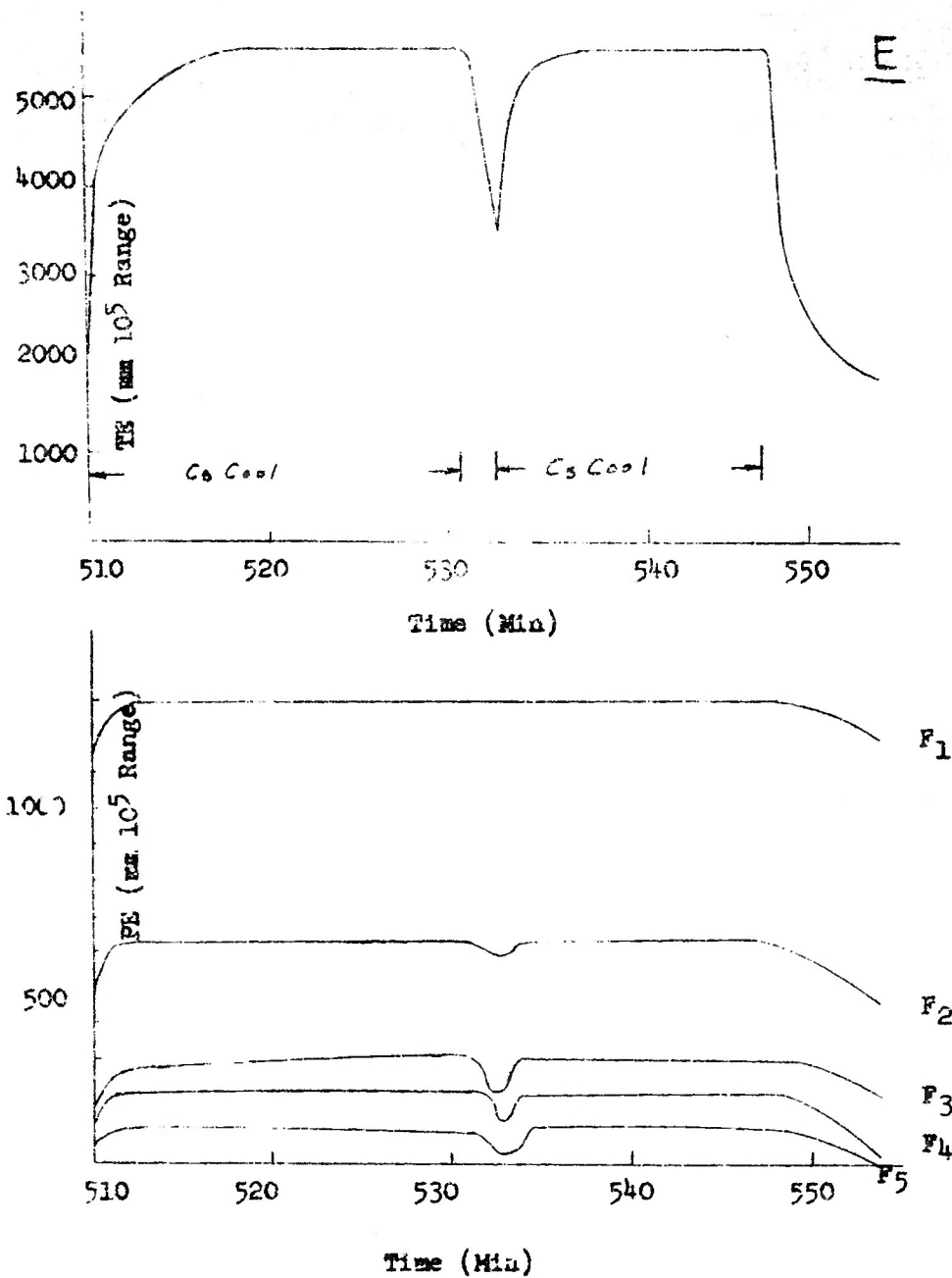


FIG. 19 E. (Continued)

thermionic emission.

As the second maximum in thermionic emission is approached, cooling the cesium source results in a rapid increase in both the thermionic and photoelectric emission, followed by a slow decrease. The rate of decrease of emission beyond the peak value decreases on approaching the second maximum (compare Fig. 18 to Fig. 19b).

Cooling the cesium source at 510 minutes (second maximum in thermionic emission at 500 minutes) results in an increase in the thermionic and photoelectric emission to a stable maximum value as shown in Fig. 19E. The momentary warming of the cesium source at 531 minutes produced an immediate decrease in the emission. Recooling the cesium source restored the emission to the original value. Considering that the actual rate of cesium addition corresponds to the deposition of less than 7 layers of cesium per minute on the cathode at 190°C, the rapid rate of decrease of thermionic emission with warming of the cesium source is rather surprising. The cooling of the tube during the momentary opening of the oven door would contribute to a decrease; however, this must not be important since recooling the cesium source resulted in an immediate increase. Actually, the time required to place the moist cotton on the bulb is significantly longer than is required for its removal. Thus the amount of cesium required to depress the emission of the "stable" surface at 190°C is very small. It is shown in Fig. 19E that this addition of cesium practically eliminates the  $F_5$  sensitivity; thus the long wavelength limit shifts toward the visible upon the addition of a small amount of cesium.

At 548 minutes the cesium addition was resumed, and within 2.5 minutes the thermionic and photoelectric emission had declined to values less than existed at the second maximum in thermionic emission. Cesium addition was continued for approximately ten minutes and the cesium source recooled. The thermionic and photoelectric emission again increased to the maximum values, but at a slightly lower rate than at the previous cooling (10 minutes compared to 8 minutes to obtain maximum emission). The entire tube was finally cooled to room temperature, producing a further increase in infrared sensitivity as discussed in the following section.

The changes observed during the cooling of the cesium source at 150°C are illustrated by the data for PT53 as shown in Fig. 20. During the initial fabrication of PT53 the cesium source was cooled at 0.57 (Cs/O) and 1.60 (Cs/O). In contrast to the tubes fabricated at 190°C, both the thermionic and photoelectric emission rapidly increased toward "stable" maximum values. In addition the ( $F_1$ - $F_2$ ) response is observed to increase to a greater degree than the  $F_2$  response. Thus there is occurring a significant increase in the photoelectric emission at wavelengths shorter than approximately 900 m $\mu$ .

A comparison of the relative photoemissions for the two (Cs/O) ratios is shown in Table VII. These data suggest that the spectral response curves of the two surfaces, 0.57 (Cs/O) and 1.60 (Cs/O), have the same shapes.

In the preparation of PT51 at 150°C it was observed that, at 0.33 (Cs/O), cooling the cesium source results in a rapid decrease in emission whereas at 0.66 (Cs/O) the emission increases steadily to a limiting value. It is of interest to note that in Sayama's study of the vapor pressure of cesium over the Ag-O-Cs surface at 145°C, the cesium pressure was less than 10<sup>-10</sup> mm Hg during cesium addition for (Cs/O) less than 1.4.

The foregoing experiments become understandable on the basis of the hypothesis that a thin layer of cesium collects on the cathode surface. As long as cesium flows into the photocell a steady state concentration is maintained on the surface because the reaction of this surface film with the solids on the interior is slow. According to this view the removal of cesium from the vapor phase is not the slow step. Instead, cesium is rapidly adsorbed on the surface from the vapor. It is the subsequent reaction of the adsorbed layer which is slow. This view is supported by Sayama's measurements of cesium pressure within the cell during the addition of cesium to a photocathode. The pressures obtained are so much lower than the vapor pressure of liquid cesium (several orders of magnitude) that rapid removal of cesium from the vapor is clearly indicated. The observation, at 190°C, that stopping the cesium flow causes first a rise and then a fall in thermionic emission strongly indicates the existence of an optimum concentration of adsorbed cesium. Departure from the optimum concentration, either above or below, causes a reduction in thermionic emission.

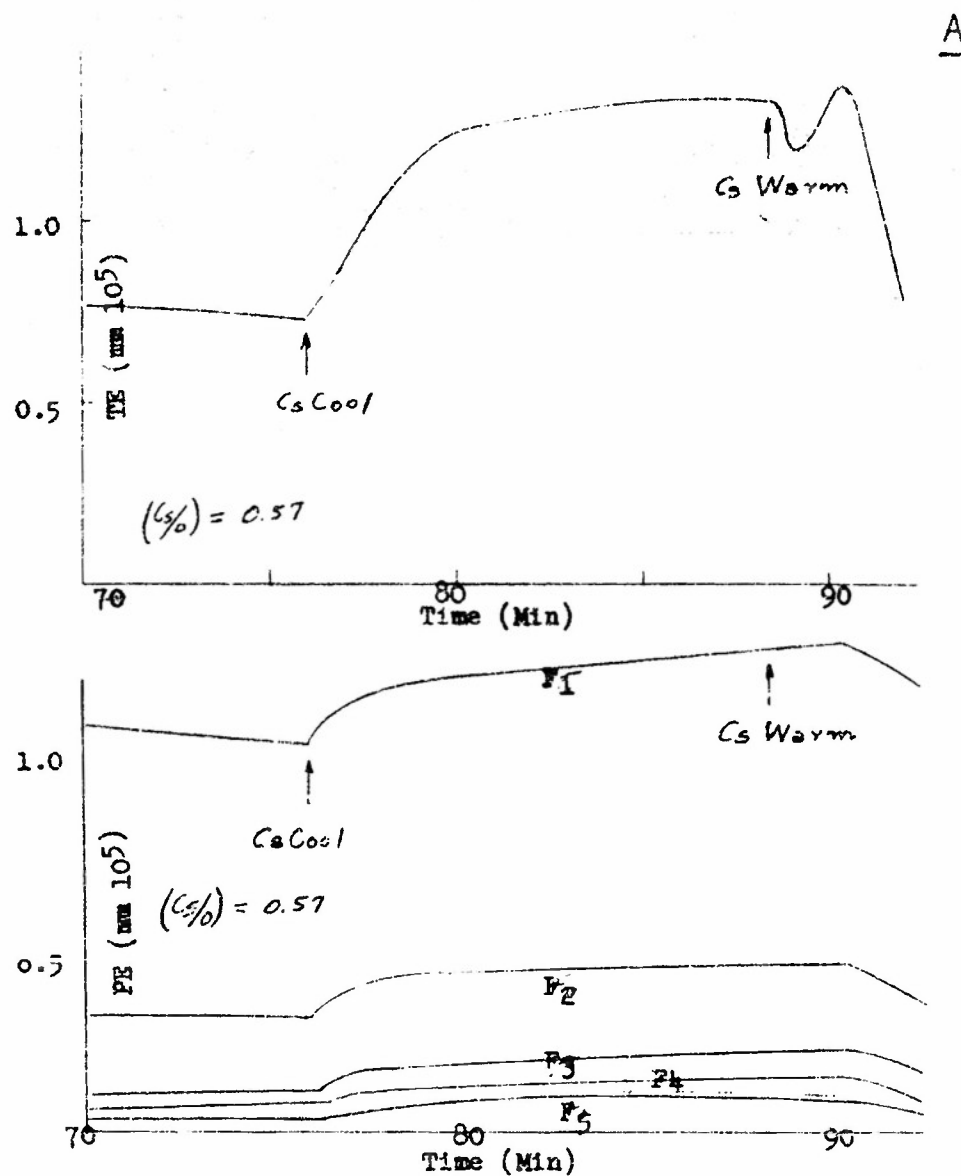


FIG. 20 A. EFFECT OF CESIUM SOURCE COOLING AT 150°C - PT53.

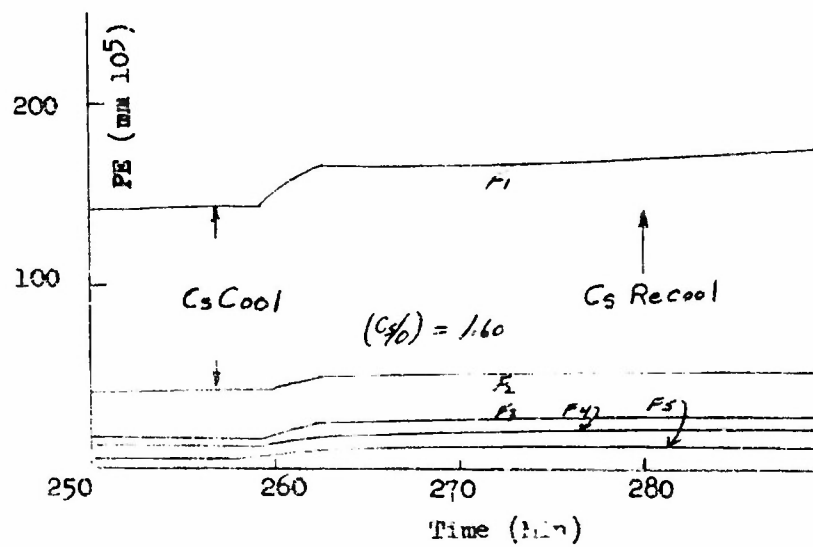
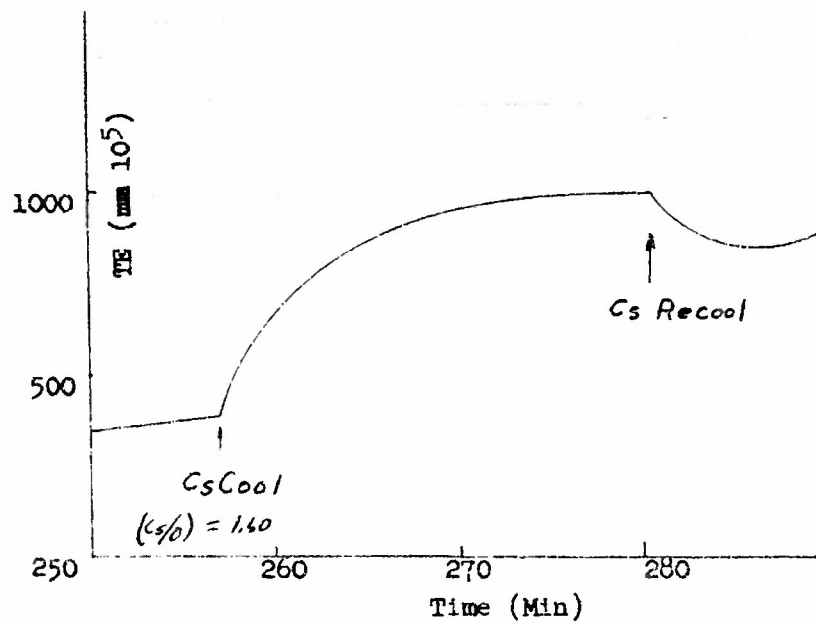


FIG. 20 B. (Continued)



TABLE VII. EFFECT OF CESIUM SOURCE COOLING  
ON RESPONSE AT 150°C. PT53

(Cs/O) Stage		$F_2/F_1$	$F_3/F_1$	$F_4/F_1$	$F_5/F_1$	White Light ( $F_1$ ) Response (mm $10^5$ )
0.57	Before Cool	0.294	0.103	0.065	0.035	1.07
	After Cool	0.332	0.161	0.103	0.061	1.31
1.60	Before Cool	0.262	0.115	0.078	0.048	159.0
	After Cool	0.333	0.116	0.125	0.066	180.5

It seems necessary at this point to comment more fully on the terms "adsorbed cesium" and "excess cesium". If we think of a layer of cesium collecting on a particular oxide, such as  $\text{Cs}_2\text{O}$ , this does not mean that an "excess" is formed beyond the stoichiometric ratio of two atoms of cesium to one of oxygen. There is no assurance that the solid compound encountered in these cathodes possesses a composition corresponding to the exact stoichiometric ratio indicated by the formula  $\text{Cs}_2\text{O}$ . Although we have no evidence to indicate a large departure from the formula  $\text{Cs}_2\text{O}$  we have, at the same time, not established that small departures do not occur. We shall therefore use the term excess cesium to indicate an excess beyond that required for equilibrium rather than an excess beyond a stoichiometric ratio. We think of "adsorbed cesium" as constituting a surface layer of cesium deposited on a solid which may be, however, a non-stoichiometric compound. With this interpretation of "excess cesium" it must be pointed out that the amount required to constitute an "excess" may change as reaction proceeds. For the equilibrium established will depend on the phases present and as one solid phase is replaced by another the equilibrium reached will also change.

When the above mechanism was first discussed in Progress Report No. 6 it was thought that the only plausible mechanism for reaction with the adsorbed layer was by diffusion through an intermediate protective layer of  $\text{Cs}_2\text{O}$ ,  $\text{Cs}_2\text{O}_3$  or some other oxide of cesium. It has since been pointed out that the very slow decomposition of silver oxide at  $190^\circ\text{C}$  may also contribute. In this case a reaction between oxygen in the vapor phase and adsorbed cesium would be responsible for reduction of the surface concentration of cesium. It should be pointed out that the decomposition rate of silver oxide is negligibly small in comparison with the rate of flow of cesium through the capillary except possibly when the source is cool. At  $150^\circ\text{C}$  the decomposition rate is negligible under all circumstances. The reason for invoking this second possibility is discussed below.

The increase in thermionic emission to a "stable maximum" beyond  $(\text{Cs/O}) \approx 1.7$  at  $190^\circ\text{C}$  and beyond  $(\text{Cs/O}) \approx 0.6$  at  $150^\circ\text{C}$  presents problems of interpretation which are somewhat confusing. In order to show the nature of the difficulty let us suppose, momentarily, that the rate of diffusion through an intermediate layer is the sole cause of the slow cathode reaction. Then both the rise and fall of thermionic emission in Fig. 19 would be governed by the same factor. At higher  $(\text{Cs/O})$  ratios, and consequently at larger thicknesses of intermediate layer, the rate of reaction of

the adsorbed cesium layer should be reduced. Consequently both the rise and the subsequent decline in thermionic emission should be slower. Inspection of Fig. 19 indicates, however, that the rate of rise in thermionic emission does not greatly change as the (Cs/O) ratio increases but the rate of decline becomes markedly less at high (Cs/O) ratios. It is this fact, among others, which suggests that the rise and fall of thermionic emission are the result of the operation of two factors one being predominant in the early stage of reaction and the second in the later stage of reaction. The suggestion that a slow thermal decomposition of silver oxide is involved was made in order to account for the second of the above factors; the concept of a diffusion controlled reaction being retained to account for the first factor above. Thus, as the (Cs/O) ratio increases, a stage is ultimately reached at which silver oxide has largely reacted and the fall in thermionic emission no longer takes place. On the other hand as long as  $(Cs/O) < 2$  some cesium oxide, containing more oxygen than  $Cs_2O$ , must be present (perhaps  $Cs_2O_3$ ) and the rate of reaction of cesium with this oxide is still slow. This reaction could still account for the partial reaction of adsorbed cesium which in turn accounts for the initial rise in thermionic emission on cooling the cesium source. The preceding discussion has been concerned with interpreting the reactions at  $190^\circ C$ . At  $150^\circ C$  it is found that beyond  $(Cs/O) = 0.6$  thermionic emission rises to a "stable maximum" and does not decline when the cesium source is cooled and maintained cool for periods up to about a half hour. Very long periods have not been studied. This fits nicely into the above mechanism since the decomposition of silver oxide is negligibly slow at  $150^\circ C$ . For the sake of clarity the mechanism discussed above has been made more specific than is really necessary. It is only necessary that two factors be operative whose relative importance changes with both (Cs/O) ratio and with temperature in the manner described above. In particular it is obvious that a thermal decomposition of silver oxide and subsequent reaction of oxygen gas with the surface layer is not essential to the mechanism. The existence of a silver oxide below a protective layer of a higher cesium oxide would be equally satisfactory provided diffusion occurs through the intermediate layer. The data probably do not justify a more detailed interpretation.

There is one more item which deserves consideration. Merely cooling the cesium source does not completely halt the flow of cesium although it is greatly reduced. It might nevertheless seem possible that the rate of cesium

addition even with the source cooled might be sufficient to maintain the concentration of adsorbed cesium at its optimum value especially in the later stages of reaction. At 190°C, however, the cesium flow rate with the source cooled is only sufficient to introduce 0.01 cathode monolayers per minute. Other experiments, to be described later, show that 0.01 monolayer is not enough cesium to markedly affect photosensitivity even at room temperature where the reaction rates are negligibly slow. At 190°C, where reaction rate is much faster, this amount of cesium does not seem sufficient to account for the observations. At 150°C the flow rate with cooled source is about six times larger because a larger capillary was used in order to obtain a flow rate, with heated source, nearly the same as that at 190°C. This amount of cesium might be sufficient to influence the results but not enough to account for the whole difference between the observations at 190°C and 150°C.

Since the above mechanism proposes that a steady state concentration of adsorbed cesium is built up during cesium addition we might expect that the results would be influenced to some degree by changing the cesium flow rate. This was investigated with tube PT49 prepared at 190°C using a larger diameter capillary than for PT47. In the case of PT49 the cesium flow rate was  $38.8 \times 10^{-8}$  moles/min. and  $3.5 \times 10^{-5}$  moles of oxygen were taken up on glow discharge oxidation. The cesium source was cooled several times during cesium addition so the composition determinations are somewhat rough. Allowing, however, for the time during which the source was cooled and for oven warm up time, maximum thermionic emission was obtained at  $(Cs/O)=1.77$ . The time required was 180.5 minutes including the 21 minutes that the cesium source was cool. The net time to reach the maximum was 139.5 minutes, correction being made for time of cooling of cesium source and for oven warm up time. Only one maximum was found. A first maximum such as that of Fig. 15 was not observed.

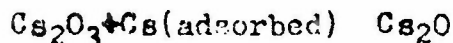
Up to  $(Cs/O)=0.87$  in PT49 cooling the cesium source resulted first in a rise in thermionic emission and then a fall similar to Fig. 19. At  $(Cs/O)=0.87$  a slow decline in thermionic emission set in only after the cesium source had been cool for 5 minutes while at  $(Cs/O)=1.17$  no decline was observed even after 10 minutes. The latter observation was made at a stage of processing roughly comparable to that for PT47 shown in Fig. 19C. In Fig. 19C the decline in thermionic emission is clearly evident within 3 minutes. The difference here is probably due to the increase in cesium flow rate. The concentration of the adsorbed cesium

layer is undoubtedly much greater in PT49 and moreover, the reduction of silver oxide probably proceeds faster. Nothing in this behavior contradicts the mechanism proposed above. Cooling the cesium source for PT49 after the thermionic emission maximum was passed resulted in an emission increase of more than six fold whereas for PT47 the increase was less than three fold. This again points to more cesium in the adsorbed layer of PT49 than for PT47 as would be expected from the higher flow rate. It was also found for PT49 that cooling the cesium source caused a large increase in  $F_2$  response (two or more slightly beyond  $(Cs/O)=1.8$ ) but very little change in  $F_1-F_2$ . In fact the  $F_1-F_2$  response was nearly constant beyond  $(Cs/O)=1.5$  whether the cesium source was cool or not. This illustrates again that the adsorbed cesium layer chiefly affects the infrared response of tubes prepared at  $190^\circ C$ . Both visible and infrared responses are affected in tubes processed at  $150^\circ C$  the effect on infrared response being more pronounced.

We must also mention that other investigators, e.g. Campbell<sup>20</sup> and Sayama<sup>21</sup>, have remarked that thermionic emission increases on cooling the cesium source after maximum thermionic emission is passed. They attribute this to the distillation of cesium back from the cathode into the source. Our experiments show, however, that this cannot be correct since thermionic emission rises whether the cesium source is cooled before or after the maximum thermionic emission. Moreover, Sayama's cesium pressure measurements show that the pressure in the photocell is too low to permit back distillation. The evidence in favor of slow cathode reactions is, in our opinion, overwhelming.

In conclusion it seems worthwhile to describe a tentative chemical picture of a finished infrared-sensitive photocathode based on the results of the present section and those of Section 3.11. The results shown in Figs. 15, 16, 17 suggest that  $Cs_2O$  is essential for photoelectric and thermionic emission since the currents are small until the composition  $Cs_2O_3$  is passed and become small again when the composition corresponding to  $Cs_2O$  is substantially exceeded. The results of the present section show that, in addition, a very small amount of cesium (adsorbed cesium) has a pronounced effect on both thermionic emission and infrared response. To obtain maximum infrared sensitivity this small amount of adsorbed cesium must be near the optimum. It is implied from the previous discussion that once silver oxide is completely reduced, at  $190^\circ C$ , then this optimum

amount of adsorbed cesium is attained quickly on stopping cesium flow and is retained for fairly long periods even when the cathode is kept at 190°C. Moreover, if cesium addition is stopped near the maximum in thermionic emission the (Cs/O) ratio is significantly less than 2. Hence for such a cathode some other oxide of cesium, such as  $\text{Cs}_2\text{O}_3$ , must be present. The picture then is of a cathode containing  $\text{Cs}_2\text{O}$ ,  $\text{Cs}_2\text{O}_3$  (?), a slight excess of "adsorbed" cesium, and metallic silver scattered through the oxides which form the cathode. The fact that, on cooling the cesium source, the thermionic emission rapidly approaches to an asymptotic value which then remains nearly constant for considerable periods of time (at 190°C) suggests that equilibrium is reached. In order to account for the rise in thermionic emission on cooling the source it is necessary to assume that one cesium oxide ( $\text{Cs}_2\text{O}_3$ ?) reacts with cesium to form  $\text{Cs}_2\text{O}$  which is known on chemical grounds to occur. The implication then becomes strong that this higher oxide functions as a "regulator" which oxidizes cesium to a sufficient degree to achieve, or nearly achieve, the optimum concentration of adsorbed cesium. In other words the chemical equilibrium



is established. The higher cesium oxide is probably not the source of photoelectrons since a photocathode carried only to the composition  $\text{Cs}_2\text{O}_3$  does not exhibit either thermionic emission or infrared sensitivity.  $\text{Cs}_2\text{O}$ , mixed with silver and having adsorbed cesium atoms, is then indicated as the source of photoelectrons. Nevertheless the higher oxide seems to have a useful function as the "regulator" which fixes the amount of residual adsorbed cesium at the proper value to provide maximum (?) sensitivity. On the basis of this view it is easy to see why silver oxide must be completely reduced. For investigation has shown that the oxide produced in the glow discharge is a powerful oxidizing agent probably capable of reducing the cesium concentration to such a degree that concentration of the adsorbed layer is below optimum. Hence it must be completely removed (at 190°C) or the rate of reaction slowed down by lowering the temperature (to 150°C).

An obvious means for testing this picture is to increase the (Cs/O) ratio for the photocathode beyond 2. Then it seems, at first sight, that infrared sensitivity would be permanently lost, if the above view is correct. For the higher oxide would then be completely reduced and a large excess of cesium would remain on the cathode.



When this test is actually applied, however, a number of complicating factors arise. In order to illustrate one of these we consider the results obtained on tube PT53 fabricated at 150°C. It is evident from Fig. 17 that continuous addition of cesium to a photocell at 150°C results in a low infrared response once the (Cs/O) ratio exceeds 2 and this seems to agree with the hypotheses outlined above. In PT53, however, the addition of cesium was continued to a (Cs/O) ratio of 2.8 where a semiconducting film collects on the tube envelope. Cesium addition was interrupted at various points and the tube was baked with the cesium source cool until thermionic emission rose. The tube was then cooled, the spectral response determined with the Beckman spectrophotometer, and then it was heated again and cesium addition resumed. This was repeated eight times six of these being beyond (Cs/O)=2. In each case the thermionic emission rose on baking and the spectral response curve obtained for the cool tube was typical of a good infrared-sensitive photocathode. This behavior is certainly not explained by the simple hypothesis outlined above. When this experiment was first performed it immediately raised the question of whether Cs<sub>2</sub>O might be the source of photoelectrons and it also raised the question of whether the hypothesis of Cs<sub>2</sub>O plus a "regulating" higher oxide of cesium had any validity whatever. The subsequent experimental work has, however, tended to confirm this idea and to indicate that the rather unexpected results obtained with PT53 are due to two complicating factors. The first of these involves the reaction of cesium with the tube envelope and the second involves the formation of a volatile oxide of cesium when the cathode (Cs/O) ratio exceeds 2. Both of these phenomena are demonstrated by the radiotracer investigation (Section 4.1). The manner in which these factors can cause complication is best indicated by the baking times required to recover thermionic emission and infrared sensitivity. The change in thermionic emission with time after cooling the cesium source at (Cs/O)=1.6 is shown in Fig. 208. Thermionic emission rises rapidly at first and then approaches a plateau within about 20 minutes. At (Cs/O)=2.82, however, thermionic emission rises almost linearly for a period of an hour after cooling the cesium source with no sign of approaching a limit. After an hour the thermionic emission was only 200 mm(10<sup>5</sup> range) at (Cs/O)=2.82 compared to 1000 mm(10<sup>5</sup> range) at (Cs/O)=1.6 after 20 minutes. Long baking times are therefore required when (Cs/O)>2 and within such long periods substantial reaction with glass or other tube elements is possible and is known to occur (see Section 4.1). When (Cs/O)>2 reaction with glass is promoted because of the formation of



a volatile oxide. These considerations show that the cathode reaction is indicated by the behavior of thermionic and photoelectric emission within the first few minutes after cooling the cesium source. Extended baking may, and usually does, have a pronounced influence on the photocathode but the chemical reactions which occur involve the transport of material away from the cathode and hence the results do not clearly indicate what is occurring in the cathode itself. The concept of a "regulator" which controls the amount of adsorbed cesium is apparently not rendered invalid. It is merely that beyond  $(Cs/O) \approx 2$  the "regulator" becomes the photocell envelope rather than a higher oxide of cesium within the cathode itself. At the same time, however, the reaction rate becomes much slower. Because of these complications it has proved impossible to obtain a simple and clear cut proof of the idea that a higher oxide of cesium controls the cesium excess when  $(Cs/O) < 2$ . Nevertheless, this view seems to be in accord with a considerable mass of data which has accumulated and which is described in subsequent sections. This discussion anticipates to some extent the results of subsequent sections. It is mentioned here to indicate why, in subsequent sections, so much attention has been devoted to the study of the baking process and why the results are so difficult to interpret, although they are apparently of practical importance. A number of examples which show the effect of extended baking are given in Sections 3.2, 3.3 and 3.4. These are usually hard to understand.

### 3.13 Effect of temperature on photoelectric emission

During the investigation of the development of thermionic and photoelectric emission at 150°C and 190°C a very interesting phenomenon was observed on cooling the equilibrated tube. After forming the "stable" photo-surface at the elevated temperature the tubes were rapidly cooled to room temperature. During this cooling process a marked increase in infrared response occurred. This is illustrated in Fig. 21 by the data for tubes PT47, PT48 and PT49 fabricated at 190°C.

During fabrication of PT47, PT48 and PT49 the cesium source was cooled shortly beyond the maximum thermionic emission and the tubes equilibrated at the reaction temperature with the cesium source cool.

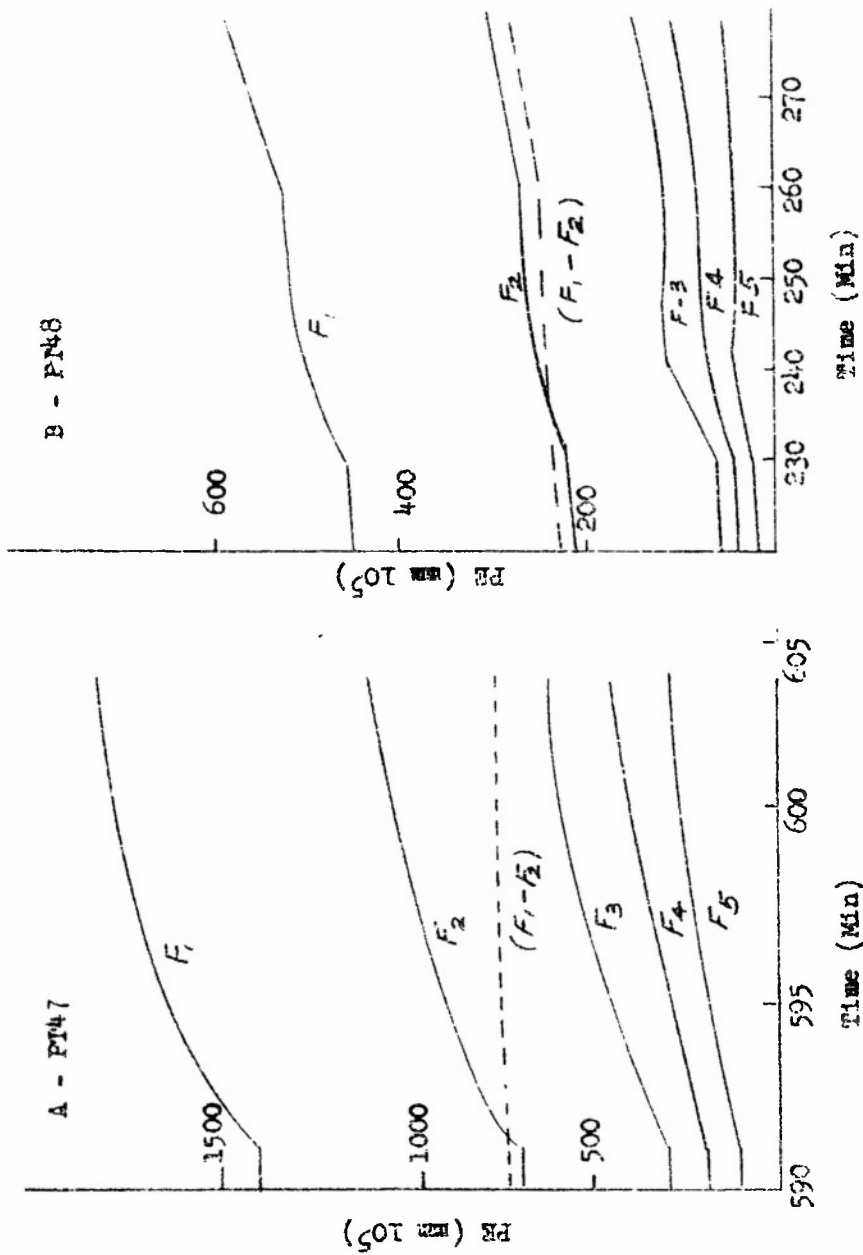


FIG. 21. CHANGE IN PHOTOEMISSION ON COOLING TUBE  
A-B FROM 190°C TO 30°C.

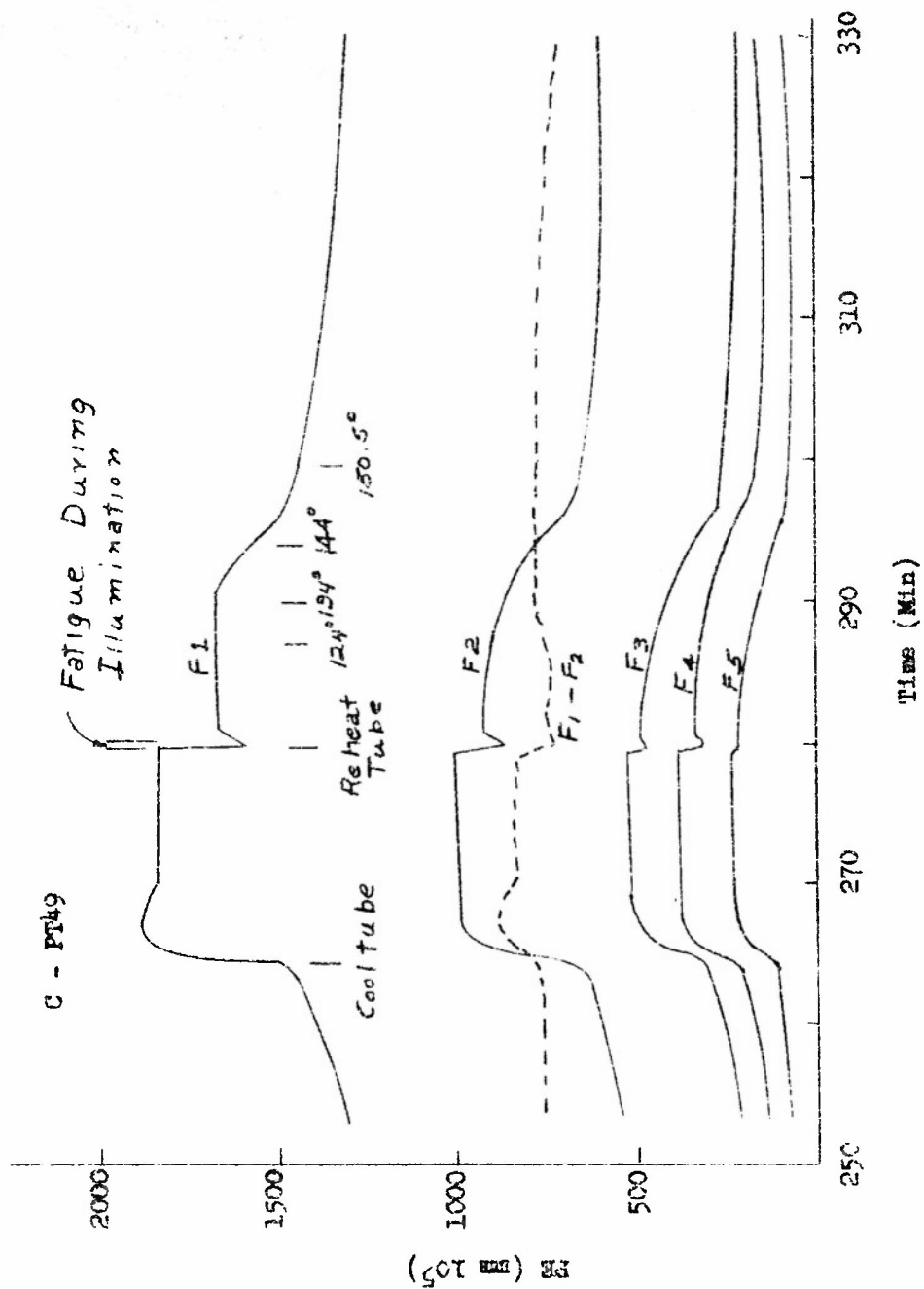


FIG. 21 C. (Continued)

After the thermionic emission and photoemission for PT47 became stable at 190°C, the entire tube was quickly cooled to room temperature by opening the oven door. During cooling there was a marked increase in the infrared response as shown in Fig. 21A. In this figure cooling of the tube begins at 591 minutes. The  $F_5$  response ( $\lambda > 880 \text{ m}\mu$ ) tripled when the cesium source was cooled at 190°C; cooling to room temperature almost tripled the response again. During this process the ( $F_1$ - $F_2$ ) response did not significantly change, and thus the changes in spectral response during cooling to room temperature are occurring primarily in the infrared region beyond 880  $\text{m}\mu$ . The cooled surface was characterized by a peak photoemission wavelength of 970  $\text{m}\mu$ , a long wavelength limit beyond 1500  $\text{m}\mu$ , and a wavelength at half maximum photocurrent of 1075  $\text{m}\mu$ .

Tube PT48 was prepared using the same glass envelope, cathode and capillary used in the preparation of PT47. The cesium flow rate was therefore the same as for PT47, namely  $7.2 \times 10^{-8}$  moles/minute. In the oxidation of PT48 only  $0.938 \times 10^{-5}$  gramatoms of oxygen was deposited. With this extent of oxidation the silver grain structure of the base was readily visible through the oxide coat. During fabrication at 190°C, the cesium source was cooled after passing the second maximum in thermionic emission. Cooling the cesium source at 190°C increased the thermionic emission from 2000 to 5450  $\text{mm}$  (105 range) and increased the  $F_2$  response from 160 to 250  $\text{mm}$  (105 range) without a very marked change in the  $F_4$  and  $F_5$  responses. This was undoubtedly related, in part, to the fact that the cesium source had been cooled several times previously. During these previous operations a marked increase in the  $F_4$  and  $F_5$  responses did occur. Thus in PT48 cooling the cesium source finally produced a change in the spectral response primarily in the 775 to 880  $\text{m}\mu$  region.

After the emission at 190°C with the cesium source cool had become stabilized, the entire tube (PT48) was cooled to room temperature beginning at 231 minutes. The cooling in this case was slowed down by varying the thermostatic control. As shown in Fig. 21B a significant increase in the infrared response was obtained on cooling to 155°C. Cooling the tube in the oven from 155°C to 140°C resulted in a slight increase in the  $F_1$  and  $F_2$  responses. The tube was then cooled to room temperature. During this period there was a further increase in the response. The final spectral response had a maximum at 950  $\text{m}\mu$ , a long wavelength limit at 1550  $\text{m}\mu$  and the wavelength at half maximum photocurrent was 1065  $\text{m}\mu$ . In the fabrication process the thermionic emission before the tube was cooled was

5700 mm  $10^5$  for PT47, and 5450 mm  $10^5$  for PT48, a difference of 4.4%. On cooling the tubes to room temperature the spectral responses of the surfaces were similar in shape but the integral sensitivity of PT47 was more than three times larger than for PT48. This again illustrates the point that there is not a 1:1 correspondence between the photoemission and thermionic emission.

In the preparation of PT49 the same cathode as for PT47 was used but the amount of oxygen deposited was increased from  $1.71 \times 10^{-5}$  to  $3.5 \times 10^{-5}$  gramatoms and the cesium flow rate was increased from  $7.2 \times 10^{-8}$  to  $38.8 \times 10^{-8}$  moles per minute. During the fabrication the cesium source of PT49 was cooled three different times after the peak in thermionic emission was passed. The thermionic emission maximum during cesium addition was 525 mm ( $10^5$  range) and before the fifth cool thermionic emission decreased to 150 mm ( $10^5$  range). On cooling the cesium source, the thermionic emission increased rapidly from 150 mm to 1250 mm ( $10^5$  range), with the  $F_1$  and  $F_2$  responses increasing from 870 to 1400 and 190 to 640 mm ( $10^5$  range) respectively. At 264 minutes (see Fig. 21C) the tube was cooled to room temperature producing the increase in photoemission shown in Fig. 21C. At the elevated temperature, as shown in Fig. 21C, the tube had not reached equilibrium emission. This photosurface on prolonged illumination through  $F_1$  and  $F_2$  filters at room temperature exhibited a "fatigue" effect. This "fatigue" produced the decreases in  $F_1$ ,  $F_2$ ,  $F_3$  and  $F_4$  sensitivity as shown at 279 minutes in Fig. 21C. During the dark period there was a partial recovery of photosensitivity. This phenomenon was not investigated in detail since it was observed to occur to a measurable degree only at this stage of fabrication of this particular tube. The tube was then reheated to 190°C with the cesium source cold. During the heating the photoemission remained relatively constant to 134°C. Between 134 and 150°C the photoemission decreased to the original 190°C values (see Fig. 21C).

After reheating PT49 to 190°C cesium was added until the thermionic emission was just replaced by a conduction current and the cesium source was recooled. The conduction current gradually decreased and the thermionic emission returned. The thermionic emission increased to a final stable value of 1050 mm  $10^5$  compared to 1220 during the previous cesium cool and 1600 mm  $10^5$  during the fourth cesium cool. This increase in photoelectric and thermionic emission at 190°C after introducing excess cesium is very

probably due to reaction of a volatile cesium oxide with the phototube envelope. The photoemission as shown in Table VIII was slightly less at 190°C than in the previous equilibrating bakes; however on cooling to room temperature, the emission increased within the experimental error to the values previously observed for the unfatigued surface at room temperature. Prolonged illumination of this surface did not produce any fatigue effect.

The final photosurface in this case was characterized by a maximum photoemission wavelength of 920 mμ, a long wavelength limit of 1300 mμ, and a half maximum wavelength of 1015 mμ. As discussed later, these emission properties are typical of a photosurface which has been exposed to excess cesium and are comparable to the normal commercial massive cathode tubes. The integral sensitivity of this tube is comparable to that for PT47.

The reversibility of the increase and decrease in photoemission with heating and cooling is illustrated in Fig. 22 by the data for the second bake at 130°C for PT55. The tube PT55 was an x-ray phase identification phototube fabricated at 190°C. Cesium was introduced to slightly beyond maximum thermionic emission and the "stable" 190°C photosurface formed. After cooling to room temperature and sealing the cesium source off, the tube was given its first stabilizing bake at 130°C to react the slight excess cesium introduced during the seal off process. The data for the baking of this tube (Fig. 22) clearly show that the change with temperature of photoelectric emission for a tube with the cesium source sealed off is reversible. The photosurface was characterized by a long wavelength limit of approximately 1400 mμ, a half maximum photocurrent wavelength of 1070 mμ, and a maximum photocurrent wavelength of 960 mμ. The spectral response of this tube after cooling to room temperature from 190°C was identical to the response after the first bake at 130°C.

An attempt was made to investigate the temperature effect using a commercial massive cathode which was characterized by a maximum photocurrent wavelength of 910 mμ, a long wavelength limit of approximately 1200 mμ, and a half maximum photocurrent wavelength of 1030 mμ. On slow heating to 190°C the following changes were observed. Initially the photoemission increased, the  $F_3$ ,  $F_4$ , and  $F_5$  responses became constant at approximately 65°C but the  $F_1$  and  $F_2$  responses increased to maximum values at approximately 115°C. From 115°C to approximately 150°C there

TABLE VIII. CHANGE IN RESPONSE FOR PT49  
ON COOLING FROM 190°C TO  
ROOM TEMPERATURE

Stage	F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	F <sub>4</sub>	F <sub>5</sub>	Thermionic Emission
	← mm 10 <sup>5</sup> →					
After fourth Cs cool	1480	660	300	205	100	1600
After fifth Cs cool	1400	620	260	180	90	1220
At room temperature before "fatigue"	1840	1000	550	405	240	
after "fatigue"	1660	910	480	330	210	
After sixth Cs source cool	1270	560	230	155	72	1050
After cooling to room temperature	1800	1000	545	400	230	



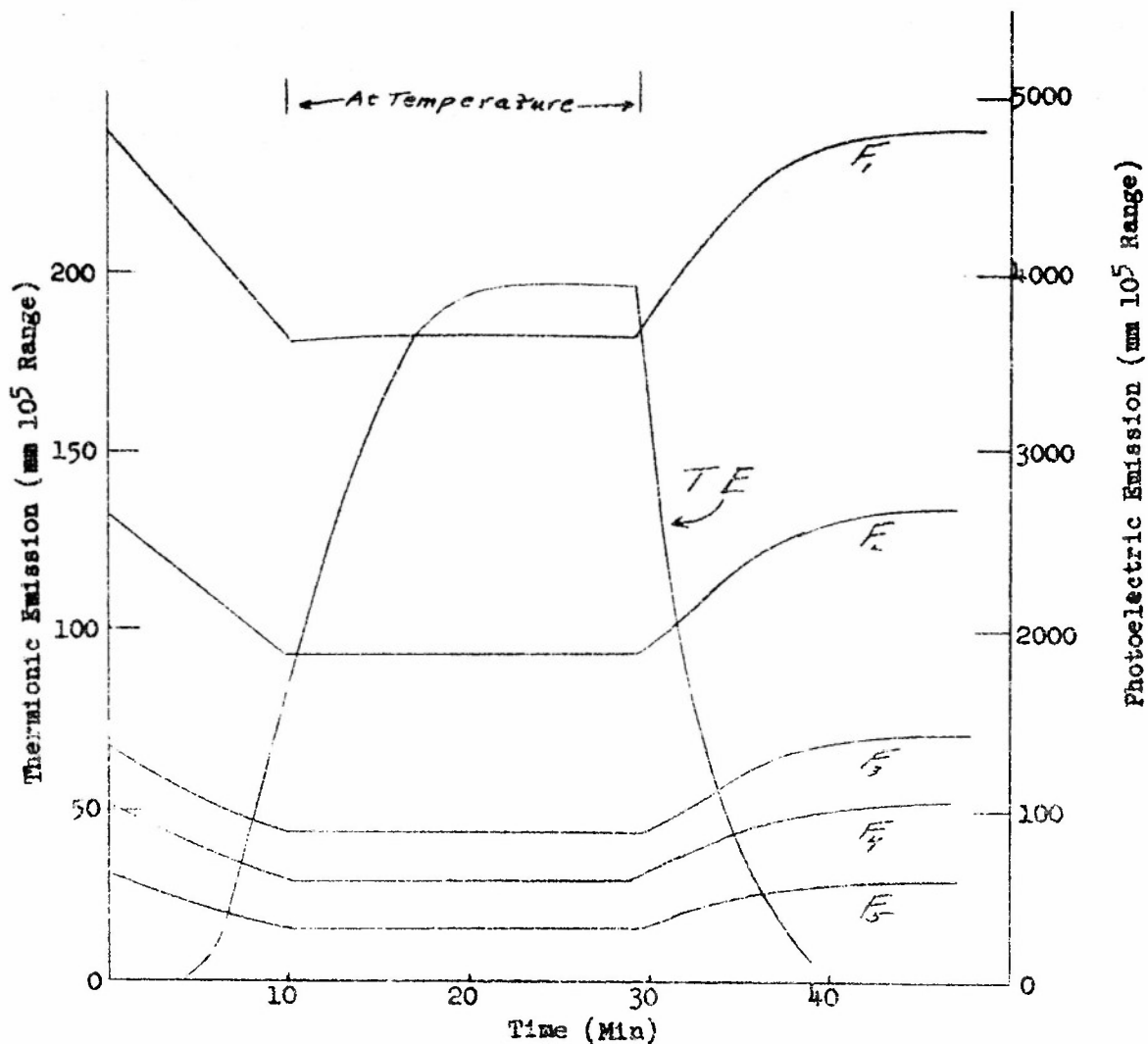


FIG. 22. REVERSIBLE CHANGE IN PHOTOEMISSION OF PT55 ON HEATING TO 130°C. AND COOLING TO ROOM TEMPERATURE. SECOND BAKE AT 130°C. CESIUM SOURCE SEALED OFF PRIOR TO FIRST 130°C EQUILIBRATING BAKE.

was a decrease in the response and an increase in thermionic emission. The change occurred primarily in the  $F_1$  and  $F_2$  responses, with only a small change in  $F_3$ ,  $F_4$  and  $F_5$ . As the temperature increased from 150°C to 190°C there was a steady decay with time and temperature in both the photoelectric and thermionic emission. Neither photoelectric nor thermionic emission was recovered on cooling to room temperature. It is clear from the above discussion that a permanent irreversible change occurred in the commercial photocathode on heating. This is very probably due to chemical reaction within the tube perhaps resulting in the transfer of cesium from the photocathode to the envelope or to a cesium "getter" within the tube. Since the previous history of the tube was not accurately known no further experiments were performed. It is clear that the above experiment on a commercially fabricated tube is not of any value in establishing the temperature dependence of photocurrent because of the complication introduced by irreversible chemical changes in the photocathode. The experiment is mentioned only to show the difficulty involved in obtaining reliable information on the effect of a variable on the photocathode. The possibility of a chemical reaction accompanying a change of temperature must always be considered. It is primarily for this reason that no quantitative systematic study of photocurrent as a function of temperature has been made. A great deal of previous experience was required before convincing evidence could be secured that chemical changes were not responsible for the temperature dependence of photoelectric emission. The example provided by PT55 (Fig. 22) conclusively shows, however, a temperature dependence of photoelectric emission which is not the result of irreversible chemical changes in the cathode.

### 3.14 Photoactivation of thermionic emission

During the addition of cesium to a massive cathode surface using the oven system of tube fabrication, a photoactivation of the thermionic emission is observed to occur. This phenomenon could not be readily studied in detail without appreciable modification of the equipment and consequently complete results have not been obtained.

The process of activation during the cesium addition is illustrated in Fig. 23 by data obtained during the early stages in the cesium addition to PT49 at 190°C. On illumination of the cathode at 78.2 minutes (TE maximum at 180.5 minutes) a marked increase in the thermionic emission occurred on illumination followed by a decay during the dark period to the original value as shown. The  $F_1$  response at this stage was 84.5 mm ( $10^5$  range). Curve 2 in Fig. 23 shows the increase in thermionic emission which was obtained on cooling the cesium source at 104.8 minutes. To a degree the process of photoactivation has an effect similar to cooling the cesium source. The process involved in the increase during photoactivation is not simple. Raising the collector voltage to a value sufficiently high to increase the thermionic emission at 190°C to a value equivalent to the combined photoemission and thermionic emission does not result in an increase in the lower voltage thermionic emission. Thus the activation process does not involve positive ion bombardment of the cathode.

In general, photoactivation is most marked during the early stages of the fabrication (i.e. low (Cs/O)) where the thermionic emission is relatively small. As cesium addition is continued the thermionic emission increases and the observed contribution due to photoactivation tends to decrease. In addition, during extended baking of the cathode, with the cesium source cool, photoactivation of thermionic emission appears to decrease. In the case of PT49 the marked effects observed may have been related to the high rate of cesium addition used compared to the other tubes studied ( $38.8 \times 10^{-8}$  moles/minutes compared to  $\sim 7.2 \times 10^{-8}$  moles/minutes).

A.H. Taylor has investigated the effect of static charges on the tube wall on the photoemission characteristic of Sb-Cs surface in small cylindrical phototubes having the cathodes and anodes at opposite ends of a short glass tube<sup>51</sup>. In these tubes it was observed that the photocurrent could be limited at low voltage by the accumulation of a static charge on the tube wall. Illumination of the tube walls using an auxiliary light source resulted in a marked increase in photoemission. This was explained by the assumption that on illumination photoelectrons may be emitted from the tube walls and the accumulation of the static charge is reduced. It does not seem probable that at the collector voltages used in the preparation of the photosurfaces used here that activation of the thermionic emission during illumination is dependent to an appreciable

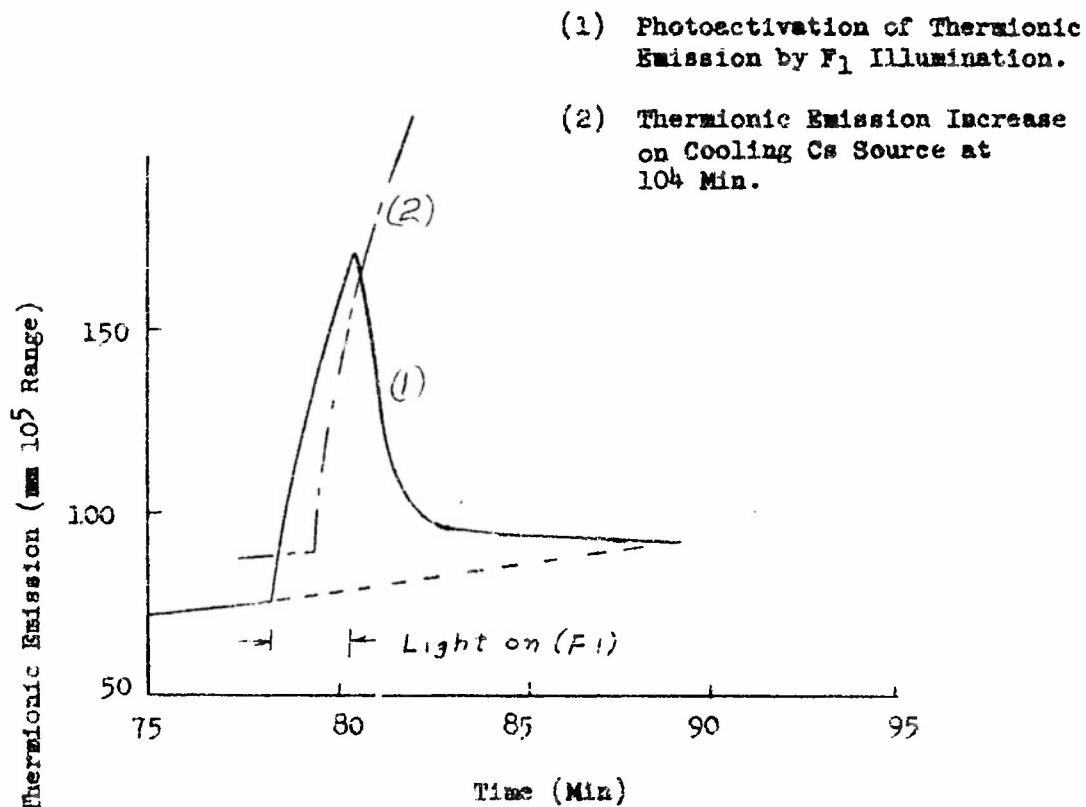


FIG. 23. PHOTOACTIVATION OF THERMIONIC EMISSION.  
PT49 (CONSTANT PHOTOELECTRIC CONTRIBUTION  
DEDUCTED FROM OBSERVED CURVE).

extent upon this effect. This possibility however has not been investigated in detail. Since on continued illumination the photoemission remained constant and photocurrent did not increase with increased voltage it does not appear probable that the effect is directly related to the presence of gas in the phototube.

### 3.15 Effect of voltage on photoelectric and thermionic emission

During the course of investigating the development of photoelectric and thermionic emission the variation of the thermionic and photoelectric emission with voltage was used to distinguish between thermionic emission and an ohmic conduction current. Generally, for convenience, the photoemission was measured at 202.5 volts throughout the run and after cooling the tube to room temperature the photoemission (on illumination through filters) was measured at 202.5 and 742.5 volts. Periodically during the cesium addition process the tube current (dark) was measured at a series of voltages with both reverse and correct polarity. This conclusively distinguishes thermionic emission from ohmic conduction. Since the phenomena observed were reproducible, data were frequently taken only at a limited number of voltages, for example 7.5, 202.5 and 742.5 volts.

During the preparation of tube PT53 at 150°C numerous observations were made on the variation of the thermionic emission at various stages of processing. The change in changes in shape of thermionic emission vs. voltage curve for this tube during the cesium addition is shown in Fig. 24A. In the early stages of processing, the current is primarily a conduction current as shown by the data at 31 minutes. As the cesium addition is continued the emission changes to a thermionic current as shown by the 44.5 minute curve and by the additional fact that reverse polarity current is nearly zero. The voltage dependence of thermionic emission near the thermionic emission maximum is shown by the 164 and 248 minute data. The linear increase in thermionic emission with increased voltage is characteristic of these tubes. The photosurfaces at room temperature in general have long wavelength limits greater than 1400  $m\mu$  and a maximum photoemission at approximately 980  $m\mu$  compared to 1250 - 1300  $m\mu$  and 910 - 930  $m\mu$  respectively for commercially available cells. After the maximum in thermionic emission

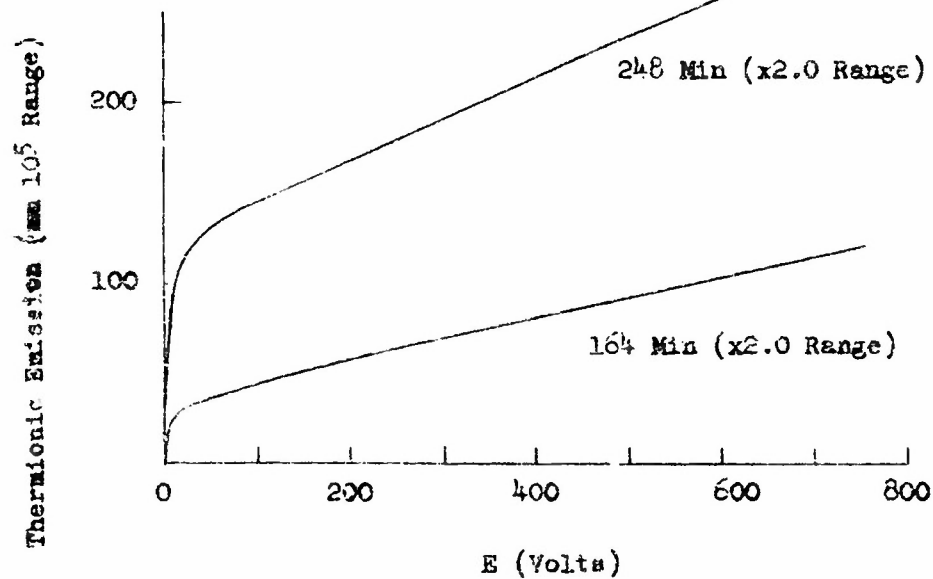
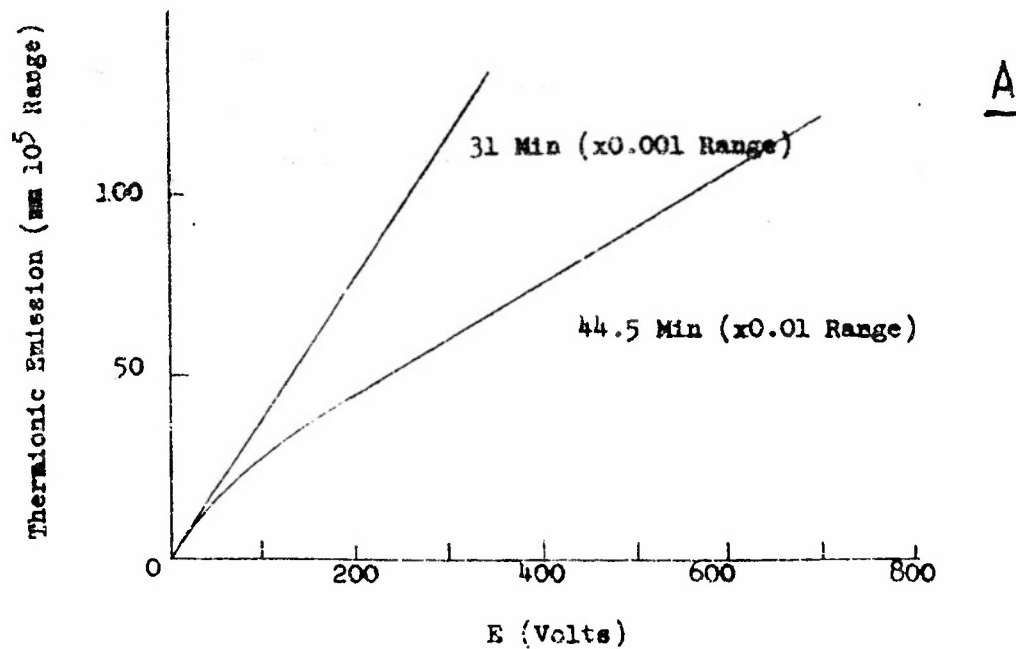


FIG. 24 A. VARIATION IN THERMIONIC EMISSION WITH VOLTAGE DURING CESIUM ADDITION AT  $150^{\circ}\text{C}$ . PT53

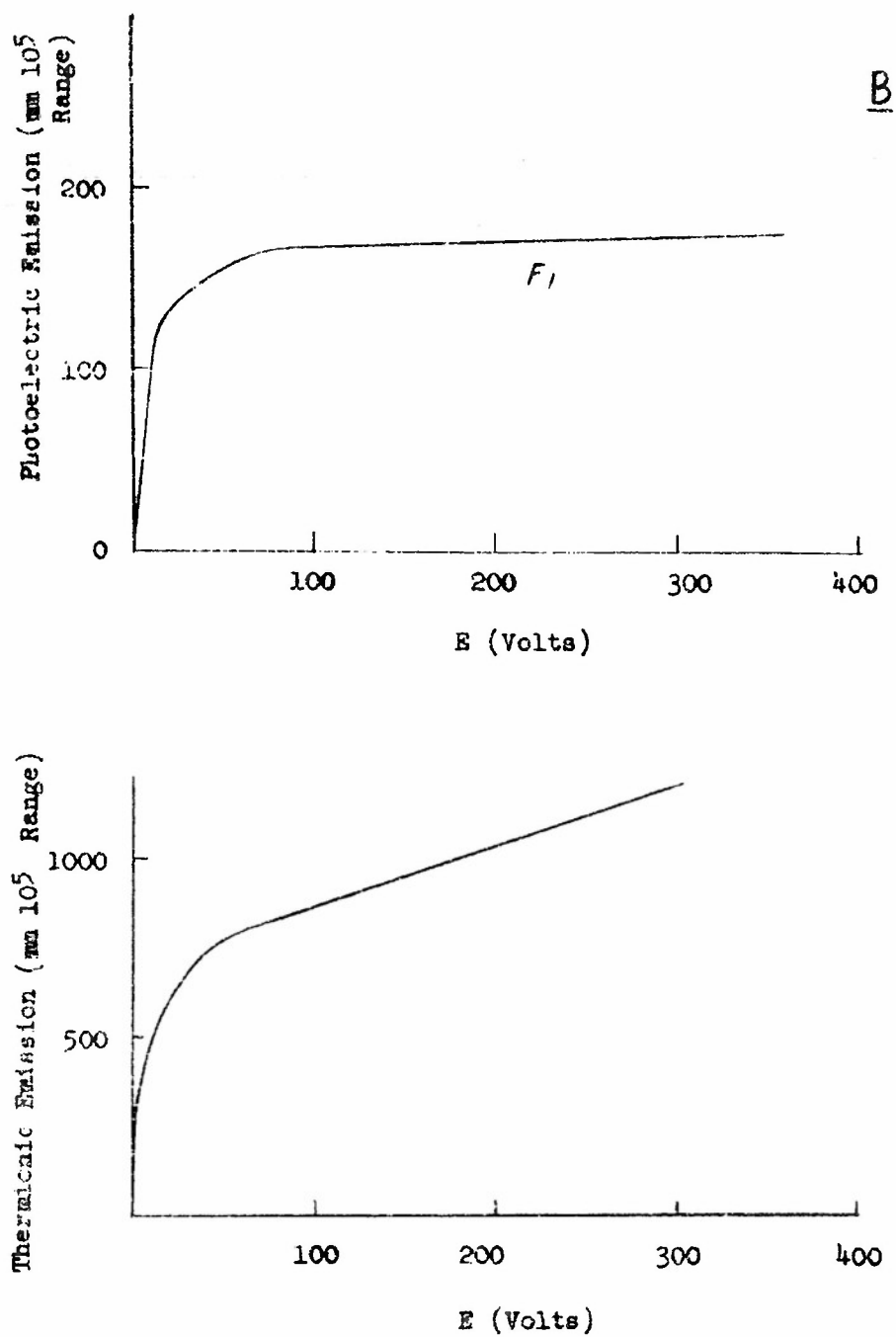


FIG. 24 B. VARIATION IN THERMIONIC AND PHOTOELECTRIC EMISSION.  
TURE AT 150°C AND CESIUM SOURCE COOL. PT53



was passed, the cesium source was cooled and the "stable" 150°C surface formed. The voltage dependence of the thermionic and  $F_1$  photoelectric response for this surface are shown in Fig. 24B. It is interesting to note that photoemission is saturated but thermionic emission is not. At this stage, it may be noted, the reverse polarity dark current was completely negligible compared to correct polarity current. Thus there is not an appreciable conduction current contribution. In addition, these characteristics are not simply related to the tube geometry since the tube used in the tracer and x-ray composition studies exhibit similar characteristics, although the geometrical arrangements are quite different.

Some variations from the behavior of thermionic emission described above are observed. During the early stages of cesium introduction, instances have been observed where the conduction, thermionic, and photoelectric emission currents increase markedly at voltages above 202.5 volts. These phenomena are undoubtedly related to the presence of a small amount of gas in the tube producing gas amplification. In certain tubes these effects could be related to the conditions of cesium addition since cooling the cesium source resulted in the emission changing to the normal behavior. In the cases where the effects could not be eliminated by the cesium source cool data obtained later in the experiment generally established the existence of a very small leak in the vicinity of the tungsten-nonex-uranium glass press seal. Results on such tubes are not considered reliable and have not been reported. Such effects were also observed when excess cesium was introduced into the tube during fabrication at 150°C and 190°C.

On rather infrequent occasions, cathodes have been obtained at particular processing stages which exhibit a high thermionic emission after cooling to room temperature. After standing at room temperature for a period of several hours this emission decreases to a low value and the current becomes a conduction current. The surface formed on PT53 after the third bake (1 and 2 at 190°C and 3 at 150°C) exhibited a rather high background emission at room temperature approximately 45 minutes after removal from the oven. The thermionic emission characteristics and spectral response characteristics of this surface are shown in Fig. 25A and B. It is to be noted that more than tripling the applied voltage produced only a 7.3% increase in photoemission at 980 m $\mu$  whereas the emission (dark) current increased 141%. The final photoresponse after

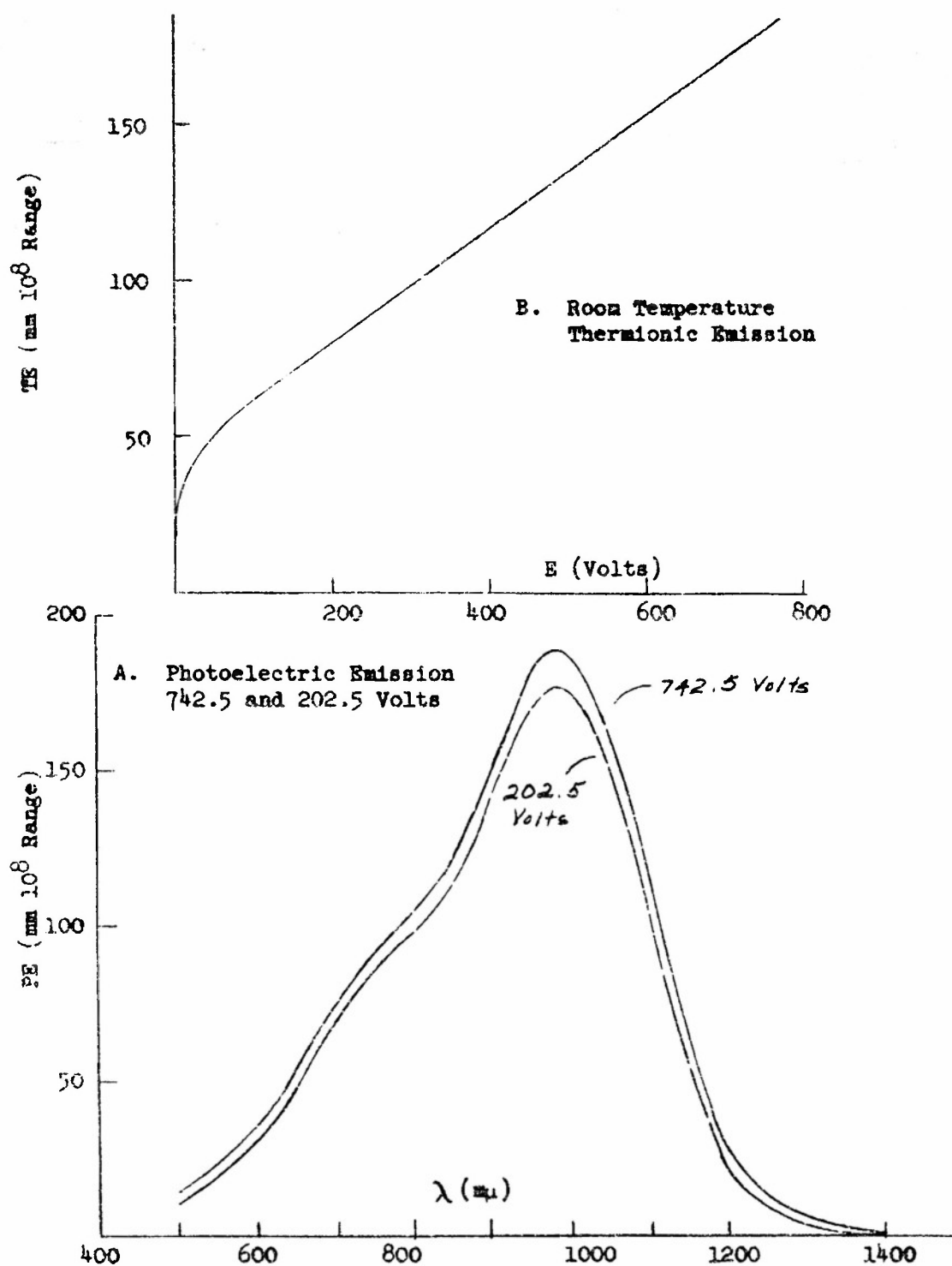


FIG. 25. VARIATION OF PHOTOELECTRIC AND THERMIONIC EMISSION OF PT53 AFTER BAKE 3 (150°C).

room temperature equilibrium was established (and the dark current became small) was identical to that obtained while appreciable thermionic emission was present. The reason for this behavior is unknown.

### 3.16 Oxide layer thickness

The relationship between the photoelectric response and the oxide layer thickness has not been investigated in detail. Such an investigation would possibly be of interest in connection with the determination of the relationship between the thermionic and photoelectric emission. In this connection it is of interest to note some results obtained during the fabrication of PT47 and PT48. In considering the results it is important to keep in mind the fact that the phenomena observed may not be considered as having general validity before more extensive experiments are performed under carefully controlled conditions.

After the preparation of tube PT47 the tube was opened, the surface and capillary cleaned, and the tube reassembled for the fabrication of PT48. It was hoped that by this procedure the fabrication process could be reproduced sufficiently closely so that the results obtained with the two tubes could be validly compared. During the oxidation of PT47,  $1.71 \times 10^{-5}$  gramatoms of oxygen were deposited on the cathode corresponding to a brilliant green color. In the case of PT48  $0.94 \times 10^{-5}$  gramatoms of oxygen were deposited. The cathode oxidation in this case was barely perceptible and the amount of oxygen deposited per unit area is comparable to the amount deposited during the oxidation of a 50% transmission silver film to 90% transmission (semitransparent cathode). The following thermionic emission characteristics during fabrication were observed for these cathodes:

	<u>PT47</u>	<u>PT48</u>
1st Maximum thermionic emission mm( $10^5$ range)	320	480
2nd Maximum thermionic emission mm( $10^5$ range)	2300	2000
Cs Cool maximum final thermionic emission mm( $10^5$ range)	5700	5450.

The shapes of the response curves after cooling to room temperature are indicated by the following data:

	<u>PT47</u>	<u>PT48</u>
Maximum photoemission $\lambda$	970	950
Long $\lambda$ limit	>1500	~1550
Maximum photocurrent $\lambda$	1075	1085

On the basis of the above results the photosurfaces present in the two tubes seem to be similar. It is shown in Fig. 26 however that the spectral responses for the two cathodes differ markedly in the photoelectric yield as a function of the wavelength. The integral photoresponse of PT48, the thin oxide surface, is considerably less than for PT47. This is also indicated by the following data on photoelectric emission on illumination through filters:

	F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	F <sub>4</sub>	F <sub>5</sub>
		mm (10 <sup>5</sup> range)			
PT47 Before cooling tube	1450	690	300	200	90
After cooling tube	1830	1120	610	445	270
PT48 Before cooling tube	460	250	80	40	20
After cooling tube	570	292	148	105	58.

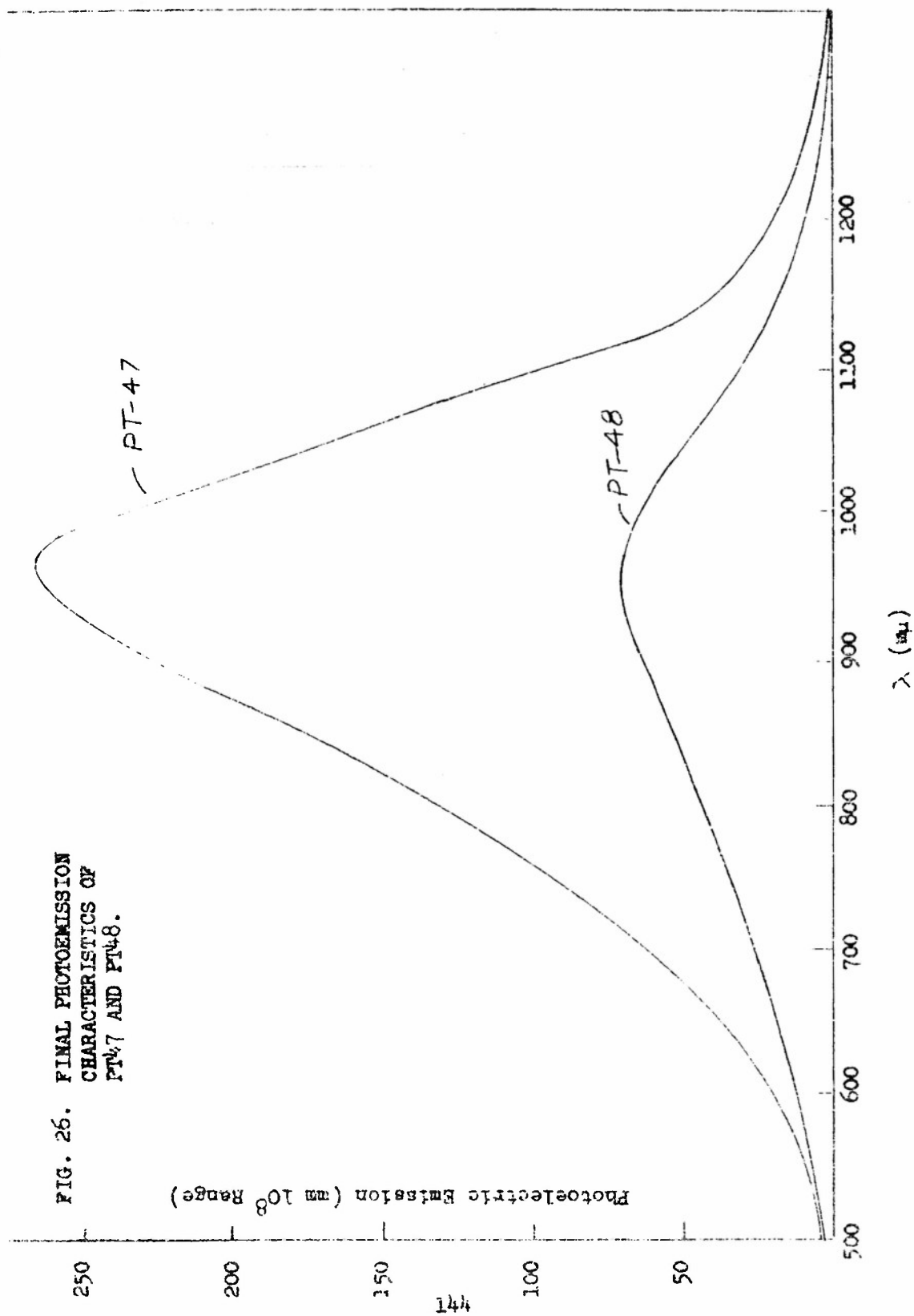
During the cooling of PT47 from 1900C to room temperature there was a much more marked increase in the infrared response than occurred in the cooling of PT48.

When the spectral responses of Fig. 26 are corrected for dispersion and lamp energy distribution they become somewhat similar to the results obtained by others<sup>29, 30</sup>. Thermionic emission is not a good indicator of final infrared sensitivity.

### 3.17 Tube geometry

In the discussion of the development of photoelectric and thermionic emission during continuous cesium addition it was stated that the presence of two thermionic emission maxima is probably related to the tube geometry. That this is the case was indicated during the investigation of the fabrication of tubes for use with a radioactive cesium tracer and also tubes for use in the x-ray identification of solid phases. The phenomena are probably best illustrated by the observations made during the fabrication of x-ray study tube PT63X.

The tube PT63X consisted of a semicylindrical silver sheet cathode which was mounted tightly against the tube wall so that only the front surface was oxidized. The tube geometry is shown in Fig. 12 Section 2.33. During glow discharge oxidation  $2.49 \times 10^{-5}$  gramatoms of oxygen were deposited over a cathode area of 26 cm<sup>2</sup>. The cathode after oxidation exhibited a brilliant green color. The cesium



addition rate was  $1.53 \times 10^{-7}$  moles per minute and cesium was added to the gross (Cs/O) ratio 2.8. During cesium addition to the x-ray phase identification tubes it had been observed that the reaction front proceeded with cylindrical symmetry from the base near the cesium source to the top of the cathode during the cesium addition. This conclusion results from the observation of cesium color. Consequently during the cesium addition to PT63X the appearance of the cathode was checked periodically.

In the majority of the tubes which have been prepared using large area cathodes the thermionic and photoelectric emission maxima occurred at (Cs/O) < 1.9. During the cesium addition to PT63X the thermionic emission did not begin to rise at an appreciable rate until the gross composition exceeded 2.0 (Cs/O). In addition, the photoelectric emission maximum appeared at 2.0 (Cs/O). On cooling the cesium source at 2.4 (Cs/O) the thermionic emission increased rapidly toward a maximum value; and the  $F_2$  photoresponse doubled. After the thermionic emission had increased to nearly the maximum value, the cesium addition was resumed. This resulted in an immediate decrease in the emission, the  $F_2$  photoresponse and thermionic emission disappearing at approximately the same time. Cesium addition was then continued until a conduction current appeared at 2.8 (Cs/O). These phenomena are illustrated in Fig. 27.

The appearance of the cathode during the processing provides a basis for explaining the unusual behavior of the tube. After a certain extent of reaction with cesium the color of the cathode changes from a brilliant green to a grey black color. After several minutes of cesium addition to the tube a reaction boundary corresponding to a transition from a brilliant green to a grey black color is formed near the base of the cathode. On continued cesium addition this boundary moves toward the top of the cathode. At (Cs/O) = 2.0 a brilliant green band approximately 1 cm wide was still present at the top of the cathode. During the cesium source cool at (Cs/O) = 2.4 the brilliant green oxide color disappeared and the cathode acquired a uniform grey black color. The final photosurface was characterized by a long wavelength limit of approximately 810 m $\mu$  and a maximum photocurrent at 650 m $\mu$ . The absence of infrared sensitivity indicates excess cesium on the photocathode (see Section 4.23 for further discussion of this tube).

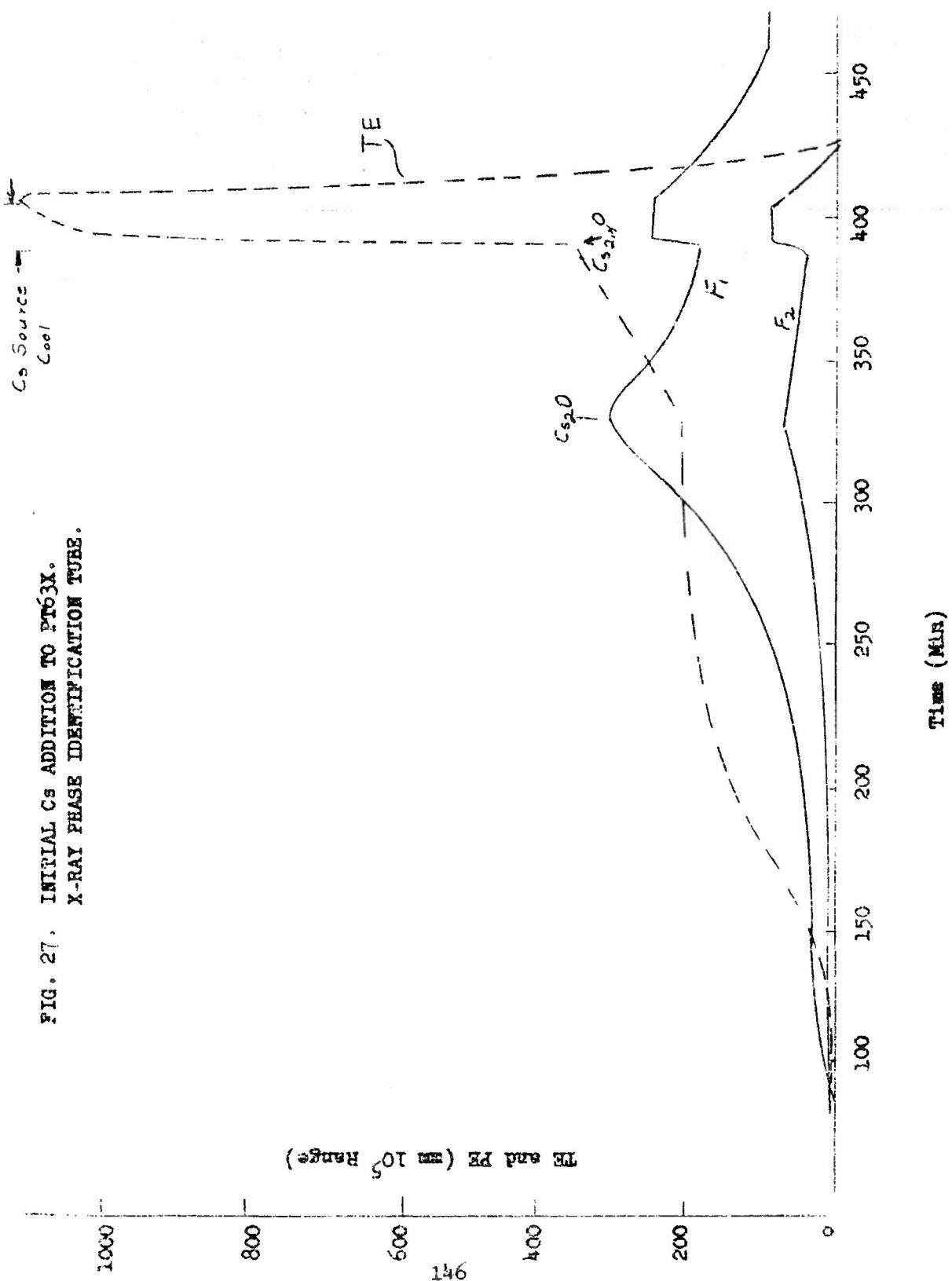


FIG. 27. INITIAL Cs ADDITION TO Pt63X.  
X-RAY PHASE IDENTIFICATION TUBE.



The observed phenomena may be interpreted in terms of the tube geometry. In the construction of the tube the cesium source inlet tube was so mounted as to provide an exaggerated case of non-uniform bombardment of the cathode by the incoming cesium. The beam striking the cathode contained a higher flux density of atoms near the base of the cathode than at the top. In addition, at least during the early stages of the cesium addition, the accommodation coefficient for cesium striking the surface must have been near unity as indicated by the observations described above.

During cesium addition to PT63X, reaction occurred to produce a heterogenous surface which was characterized by a high (Cs/O) ratio near the base, and a low (Cs/O) ratio at the top. Thus the thermionic emission plateau is the result of the slow migration of a low work function region from the base toward the top of the cathode. The width of the region increased as the top of the cathode was approached due to the flow characteristics. On cooling the cesium source, in addition to reaction of the cesium with the surface, a migration of cesium from the high (Cs/O) region to the low (Cs/O) region probably occurs. The rate of this migration would be determined by the vapor pressure of cesium over the cesium oxide phases present. After a partial equilibration of the surface, the decrease in emission produced by further cesium addition results from the formation of an excess cesium surface over the entire cathode area.

It may be noted that an excess cesium massive cathode photosurface in general has a considerably lower photoresponse than at optimum sensitivity (see Section 4.23). In addition, the spectral response curve is shifted toward the visible portion of the spectrum. The  $F_5$  response of PT63X closely parallels the behavior of thermionic emission during the cesium addition. The total photoresponse of the cathode relative to the observed thermionic emission is appreciably less than would be anticipated for a "uniform" cathode fabricated at 1500°C.

It is important to recognize that the distribution of cesium over the cathode is not entirely determined by the flux of cesium atoms arriving directly from the capillary outlet and "sticking" to the cathode on the first collision. The walls of the phototube envelope undoubtedly reflect a considerable proportion of cesium atoms which ultimately reach the cathode. The totality

of cesium atoms scattered in this way no doubt contribute to a much more uniform cathode coverage. This contribution to uniform coverage is not sufficient, in this exaggerated example, to overcome the non-uniform coverage provided by direct bombardment. The cathodes discussed in previous sections were, probably more uniformly covered because the capillary outlet was more symmetrically located relative to the cathode.

The radioactive tracer tubes are fabricated from silver bases formed by evaporation on glass discs. Hence the back surface of the cathode is shielded by glass (see Fig. 14). In the fabrication of these tubes only one maximum in thermionic emission during cesium introduction is observed.

It is also worth noting that in tubes having a nickel anode wire the wire is slightly oxidized during the glow discharge oxidation of silver. During cesium addition the anode wire develops thermionic emission and photo sensitivity. The emission characteristics of the anode wire parallel the characteristics of the photosurface. However, only a single maximum in emission is observed during the cesium addition. The anode surface does not exhibit a large infrared response but the general behavior on cooling the cesium source is the same as observed at the cathode.

From the foregoing observations it is obvious that depending upon the tube geometry a considerable variation in the thermionic emission as a function of the tube gross composition may occur. Thus, if the thermionic emission characteristics are used to control the processing, and an unsatisfactory tube design is used it is readily possible to obtain a tube which after equilibration has a poor infrared response because of the presence of excess cesium. Baking of such a cathode does not recover the infrared sensitivity unless a sink for the excess cesium is present in the tube.

It is to be noted that the above observations agree well with our previous statement that the slow step in cathode reaction with cesium is not the removal of cesium from the vapor phase. The evidence indicates, in fact, that collision efficiency is high.

### 3.18 Definition of a "normal" tube

As a result of the detailed study of the development of thermionic and photoelectric emission during

the fabrication of massive silver cathodes a set of characteristics were evolved which describe the behavior of a "normal" tube. This set of characteristics constitutes a convenient standard to which other photocathodes can be compared. The term "normal" actually means a highly infrared-sensitive cathode.

The "normal" tube is characterized by the following behavior. During cesium addition the initial current is a conduction current. When thermionic emission begins to develop the white light response quickly appears and is soon followed by an appreciable  $F_2$  response. At a slightly later stage the  $F_3$ ,  $F_4$ , and  $F_5$  responses appear. After a period of addition, and before the maximum thermionic emission is reached, cooling the cesium source results in an immediate increase in thermionic and photoelectric emission. The emission, depending upon the gross tube composition existent at that time, may at  $1900^\circ\text{C}$  decrease or increase to a stable maximum, but at  $1500^\circ\text{C}$  will definitely increase to an apparently stable value.

On further cesium addition a maximum in the thermionic emission is obtained. Cooling the cesium source at this composition results in a rapid increase in the thermionic and photoelectric emission to "stable" values. On cooling this surface to room temperature there occurs a marked increase in the infrared sensitivity of the cathode. Provided excess cesium has not been introduced into the tube, the final photosurface in terms of the standard conditions defined in Section 2.13 is characterized by a spectral response having a long wavelength limit greater than  $1400\text{ m}\mu$ , a maximum photocurrent wavelength between  $950$  and  $990\text{ m}\mu$ , and a half maximum wavelength of greater than  $1060\text{ m}\mu$ . These values may be compared to the following values observed with commercial cathodes; namely, wavelength limit  $1200 - 1300\text{ m}\mu$ , maximum photocurrent wavelength of  $900 - 930\text{ m}\mu$ , and a half maximum photocurrent wavelength of  $1000$  to  $1030\text{ m}\mu$ .

In a number of our subsequent experiments we have added cesium far beyond maximum emission and the final phototubes frequently have low infrared sensitivity. By continuously following the emission during cesium addition and by periodically cooling the cesium source we can readily recognize whether such tubes were normal at some intermediate stage.

### 3.2 "Commercial" Fabrication of Massive Cathode Phototubes

The commercial procedure for the fabrication of massive cathode phototubes is characterized by simplicity of the processing procedure. The procedure involves the oxidation of the silver cathode to the desired extent, evacuation, firing a  $\text{Cs}_2\text{CrO}_4$ -Si pellet, and then heat treating to produce the desired photo-surface. The excess cesium present is removed by exhaust into the vacuum system, or by reaction with a suitable getter such as a lead glass press seal or lead oxide or tin oxide coating on the back of the cathode.

During the early stages of the project a phototube PT24C was fabricated using a procedure which has something in common with that described above and which, for lack of better phrase, is described as the "commercial process". The detailed results obtained for this tube are presented in the following sections. It is to be noted that the spectral responses in this case are specified for a 0.32 mm slit, a collector voltage of 65 volts, the vibrating reed electrometer at low sensitivity, and a lamp voltage of 4.97 to 4.99 volts. It must be admitted that the space allotted to the description of this cathode is out of proportion to its actual importance. This is done largely because it affords an opportunity to apply the ideas developed in previous sections and also because the changes which occur on prolonged baking are made particularly evident. Approximate corrections for dispersion and lamp energy distribution have also been applied so that the effect of these factors on the spectral response is made more clear.

#### 3.21 Tube fabrication

A description of the fabrication procedure for PT24C has been presented in Section 2.31. The tube design is shown in Fig. 10. The tube consisted of a semi-cylindrical silver cathode with a centrally mounted anode wire. A dry ice-acetone trap was attached to the tube using approximately 8 mm bore pyrex tubing. After firing the  $\text{Cs}_2\text{CrO}_4$ -Si pellet the tube was sealed off the vacuum system and the trap cooled with a dry ice-acetone mixture. Since, at  $-66^\circ\text{C}$ , the vapor pressure of cesium is of the order of  $2 \times 10^{-12}$  mm Hg the trap is equivalent to having the tube mounted on a vacuum system with an excess cesium getter present. After a determination of the spectral

response the tube was subjected to a series of bakes in a quartz tube furnace at 180 - 200°C. The temperature of the tube was measured by placing a thermometer along the side of the tube and opposite the cathode surface. The trap was maintained cold throughout the processing except when excess cesium was introduced back into the tube.

From the 1st to the 13th bake the trap was maintained at approximately -68°C. At bake 13 the trap was allowed to warm to room temperature and the residual cesium diffused into the tube. After 21 hours the spectral response was remeasured and the tube rebaked (bakes 14 through 19) with the trap again immersed in the dry ice-acetone mixture.

In Table IX are presented the following data for PT24C: (1) baking time at 180 - 200°C, (2) the final thermionic emission at the end of the bake, and (3) the spectral response characteristics uncorrected for dispersion or the lamp energy distribution. The baking times used were determined by the changes which were observed in the thermionic emission during the baking process.

### 3.22 Spectral response characteristics

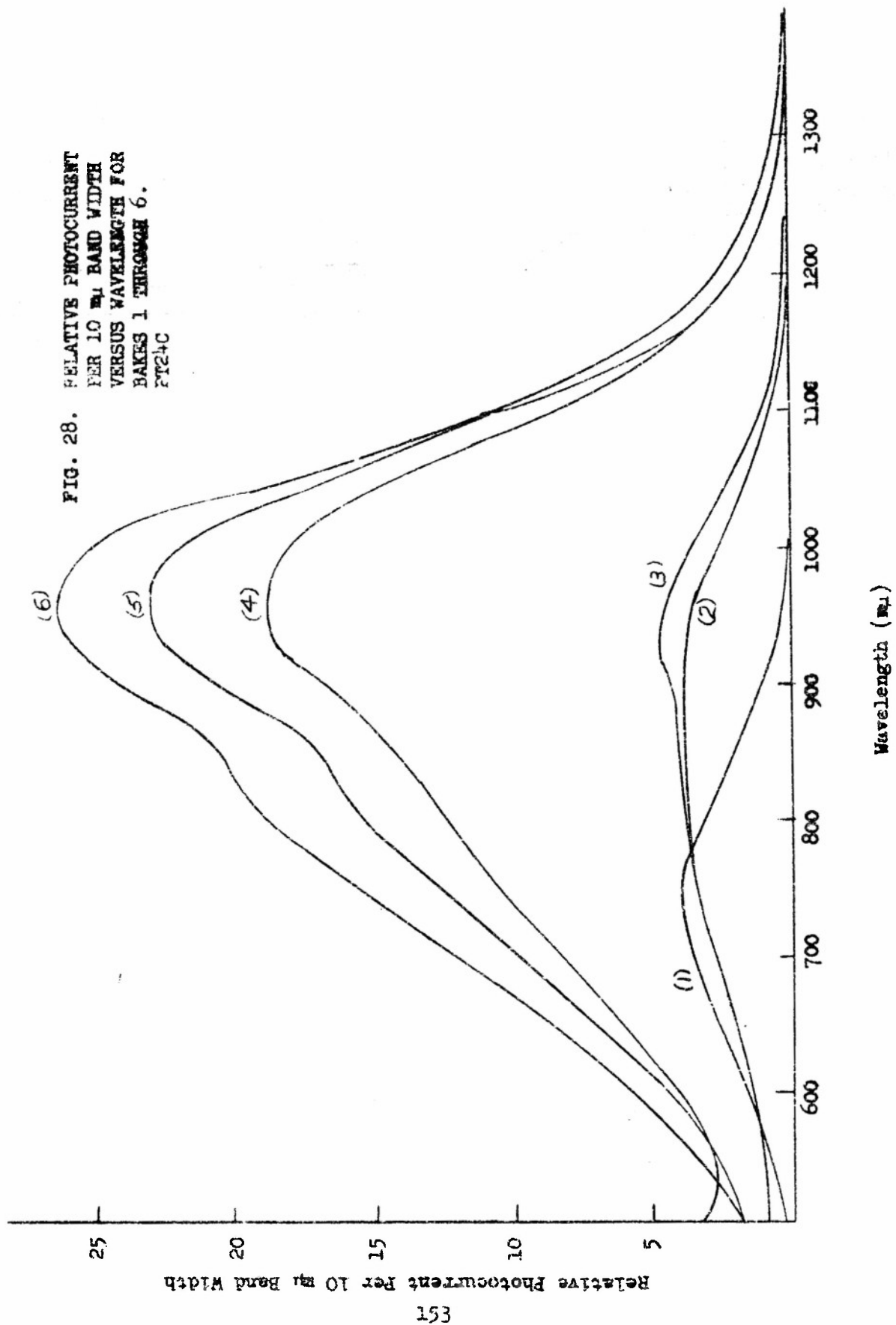
The increased spectral responses for PT24C were corrected for quartz prism dispersion and are reported in terms of a 10 mμ band width relative photoresponse. The development of maximum photosensitivity during bakes 1 through 6 is shown in Fig. 28. In Fig. 29 is shown the decline in photoemission obtained on extended baking; while Figs. 30 and 31 illustrate the effect of cesium addition from the trap followed by baking.

Initially, after the room temperature cesium addition, the maximum spectral sensitivity appeared at 515 mμ. It will appear later that this is typical of a surface containing a large excess of cesium. During the first bake the maximum shifted to 750 mμ and on the second shifted to the 900 mμ region. During the second bake the observed long wavelength limit shifted from 1075 to 1425 mμ. This operation corresponded to the 33 minute bake at 180 - 200°C. With bake 3 through 6 there was a rapid increase in the sensitivity over the entire range from 600 to 1500 mμ. The growth of the peak in the 900 mμ to 1000 mμ range and the development of an inflection in the 750 - 850 mμ region are interesting to note. The inflections suggest that two types of emitting centers are present, a point which is

TABLE IX. BAKE AND SPECTRAL DATA PT24C

Bake No.	Time at 180-200°C (min.)	Accumulated Time at 180-200°C (min.)	Final Thermionic Current, $\mu$ a	Peak $\lambda$ , m $\mu$	Long $\lambda$ Limit	Half Peak $\lambda$ Low $\lambda$ High $\lambda$	Color of Surface
0	--	--	--	515	--	552 870	reddish-grey to black
1	18	18	--	765	1075	720 1035	
2	15	33	3.9	915	1425	753 1050	
3	12	45	2.8	942	1500	806 1107	
4	18	63	120.0	990	1650	800 1100	
5	17	80	72.0	990	1600	795 1088	
6	21	101	56.0	980	1575	795 1088	dark grey to black
7	23	124	18.0	977	1550	795 1088	silver grey with dark tinges
8	42	166	12.6	940	1300	733 1030	
9	48	214	0.96	930	1300	715 1017	
10	70	284	0.096	905	1225	675 990	
11	82	366	0.013	750	1150	578 948	ivory, yellowish
12	30	396	0.003	755	1150	557 948	
13	Cs from trap; room temp. 24 hours	--	--	720	1075	600 770	
14	30	30	0.006	890	1250	682 976	
15	23	53	0.350	915	1275	703 995	
16	33	86	0.005	915	1300	712 997	
17	26	112	0.012	918	1275	690 997	
18	73	185	0.0000	910	1275	702 996	
19	120	305	0.0006	910	1250	690 996	
20	Trap and tube at room temp. 4 hours	--	--	910	1275	703 990	silvery white
21	18 hr	--	dead	--	--	--	

Data not corrected for dispersion or lamp spectral distribution.





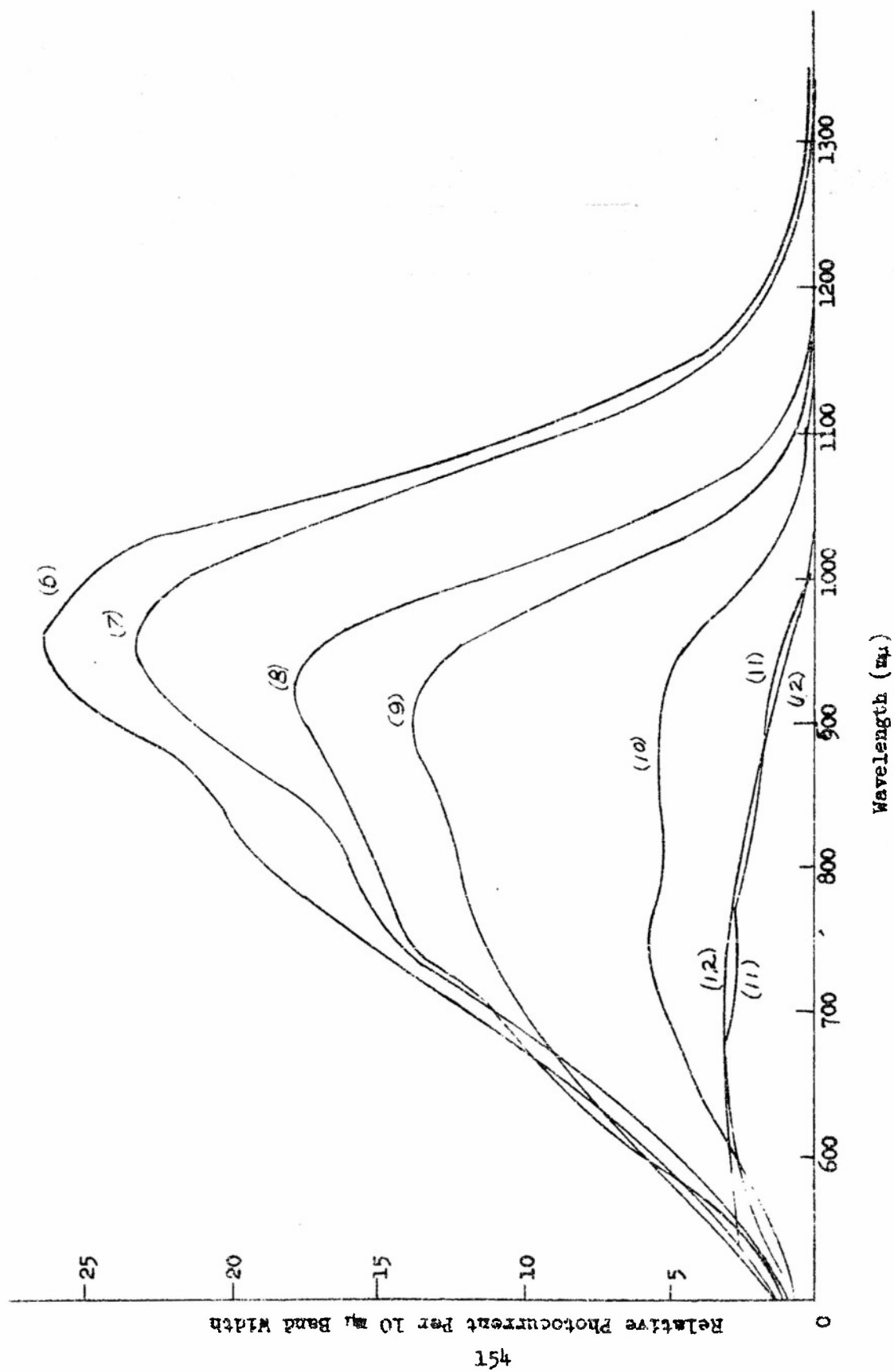
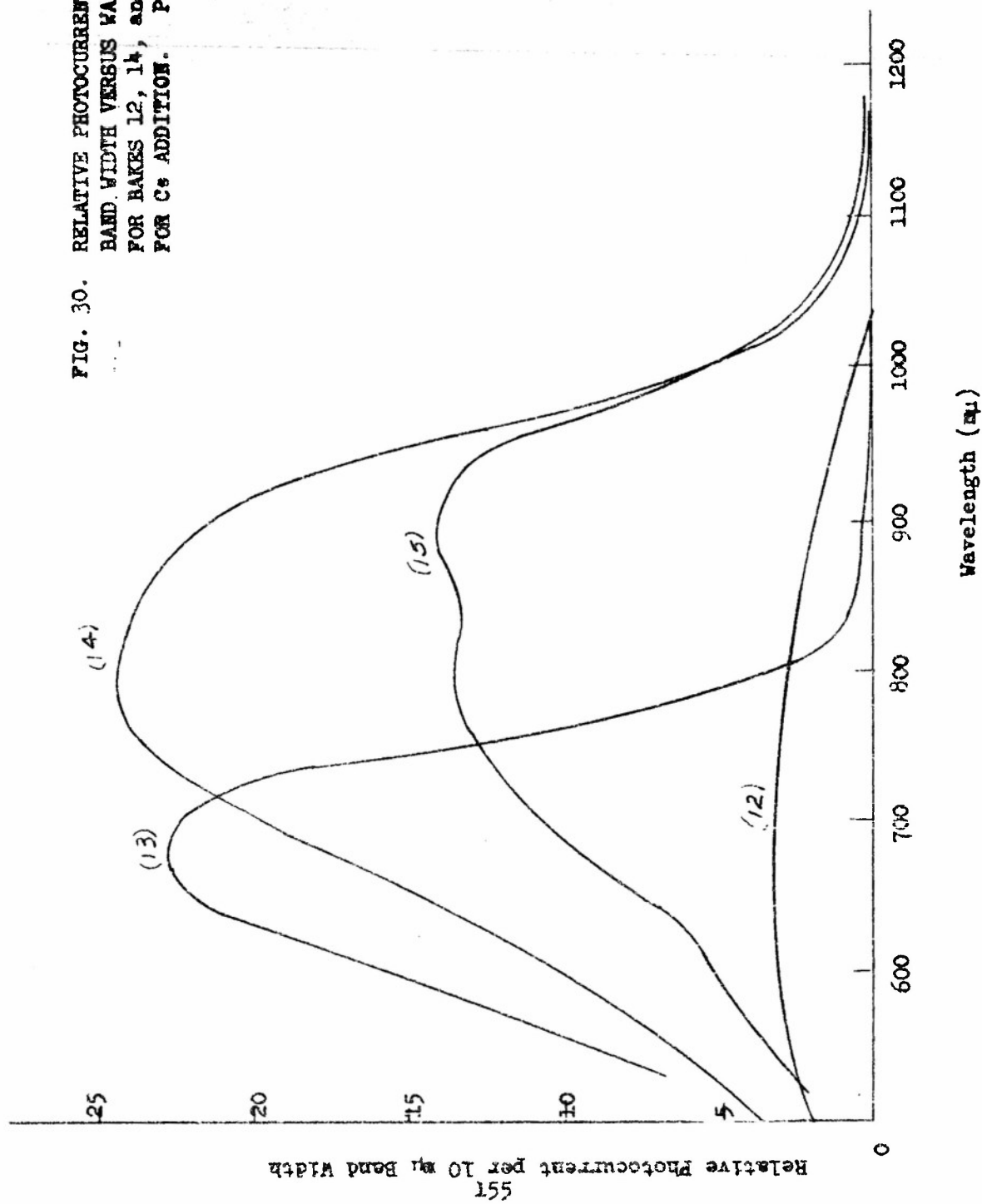


FIG. 29. RELATIVE PHOTOCURRENT PER 10  $m\mu$  BAND WIDTH VERSUS WAVELENGTH FOR BAKES 6 THROUGH 12.

FIG. 30. RELATIVE PHOTOCURRENT PER 10 mμ  
BAND WIDTH VERSUS WAVELENGTH  
FOR BAKES 12, 14, and 15; 13 IS  
FOR C<sub>2</sub> ADDITION. PT24C.



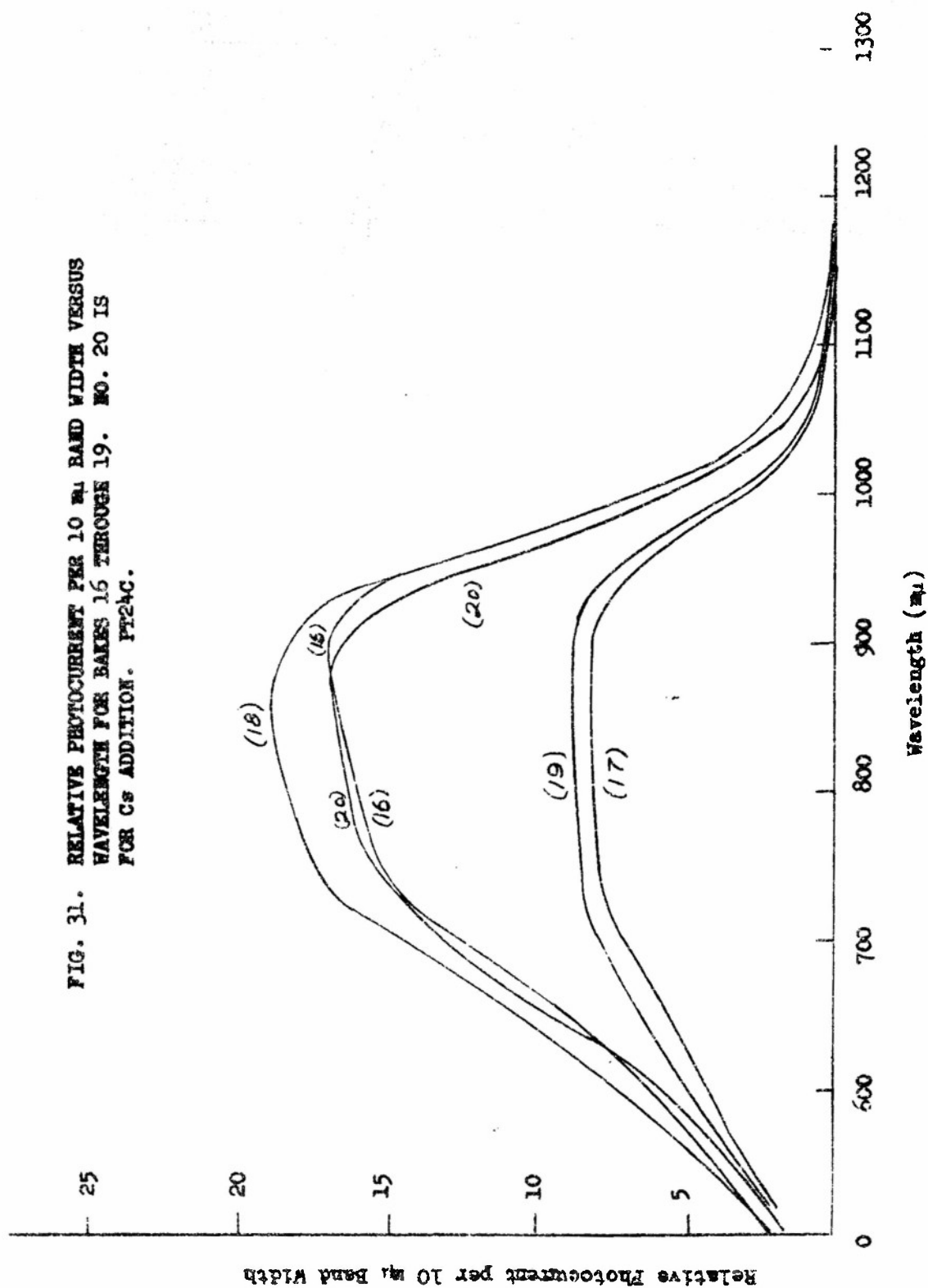


FIG. 31. RELATIVE PHOTOCURRENT PER 10  $m\mu$  BAND WIDTH VERSUS WAVELENGTH FOR BAKES 15 THROUGH 19. NO. 20 IS FOR Cs ADDITION. PT24C.

further discussed later. In addition, as shown in Fig. 28, the maximum photosensitivity corresponds to shorter long wavelength limit and lower final thermionic emission than the surface (curve 5) which had the highest thermionic emission and had a long wavelength limit near 1650  $m\mu$ .

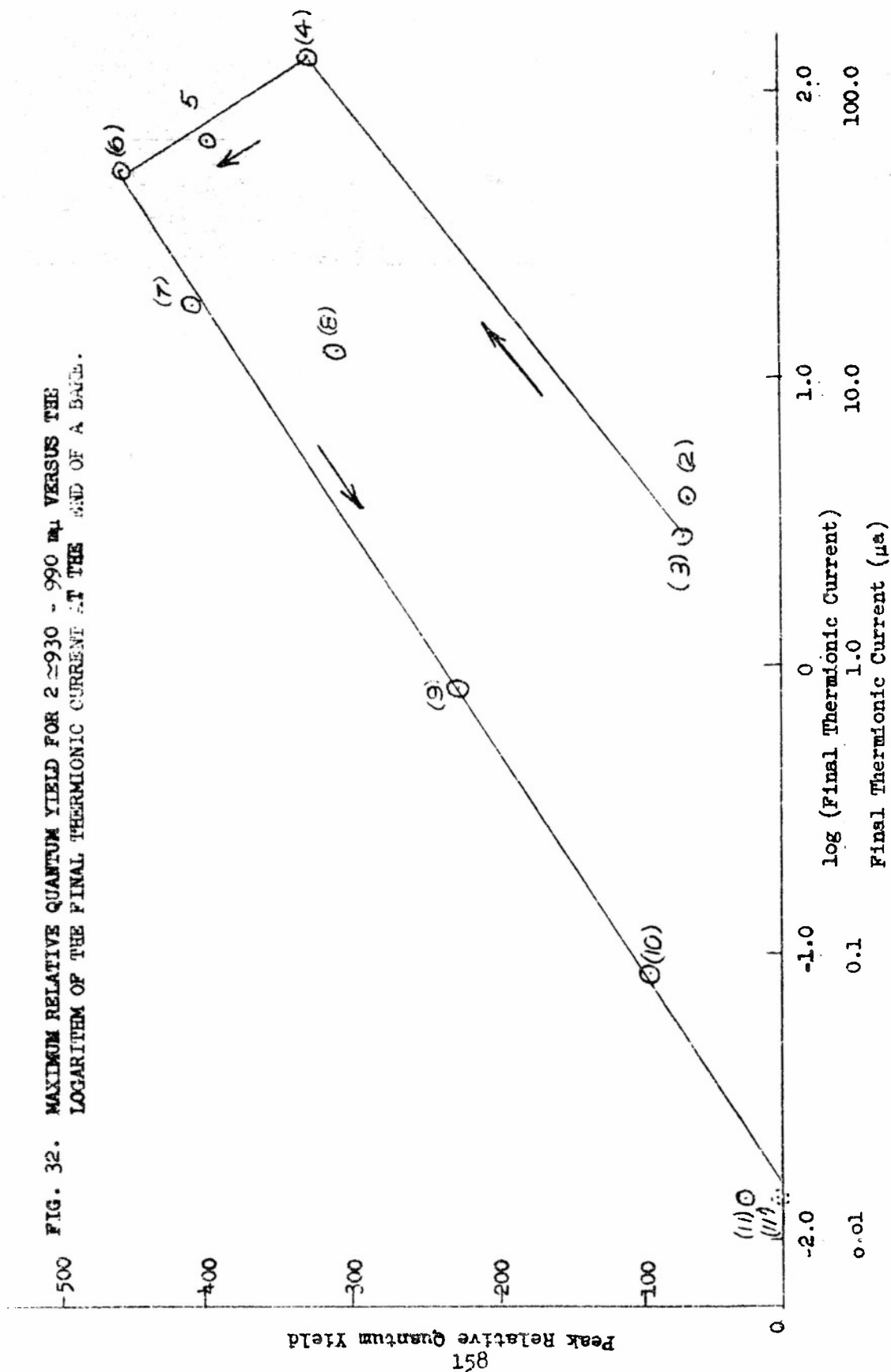
At the maximum sensitivity the cathode had changed from a reddish grey-black color to a uniform dark grey brown. As the baking was continued there was a decrease in photosensitivity as shown in Fig. 29 and the cathode changed to an ivory color which became a silvery white by the 20th bake.

At bake 13, Fig. 30, cesium was introduced into the tube by warming the trap to room temperature. This produced a very marked increase in sensitivity in the 600 - 800  $m\mu$  region. The response after cesium addition is similar in wavelength characteristics to that present after the first bake. Baking after cesium addition caused the spectral sensitivity curve to shift toward the infrared.

Further baking of the tube resulted in the set of photosensitivity curves shown in Fig. 31. The erratic behavior of the photosensitivity after bake 14 may be related to a greater variation in the sensitivity per given area. This was not checked during the processing of the tube from bakes 14 through 20. In the case of the initial set of curves 1 - 12 the variation in sensitivity with the allowed positioning of the holder corresponds to approximately a 10% variation in the total current. The form of the spectral sensitivity curves, however, was invariant with respect to the area illuminated. This would indicate that the spectral emitting surface was uniform in work function after each bake with possible variations in the volume and/or surface area of active compounds.

In the production of semitransparent photocathodes the amount of cesium to be added for the development of the optimum photosensitivity is controlled by measuring the thermionic current during the introduction of cesium. After the peak in the thermionic emission is passed the cesium addition is discontinued. The tube is then baked at 180 - 200°C for a short additional time until thermionic emission passes through a second maximum, and it is then cooled to room temperature. In the preparation of PT24C the thermionic emission during baking was measured. In Fig. 32 the logarithm of the final thermionic current at the end of each bake is plotted as a function of the

FIG. 32. MAXIMUM RELATIVE QUANTUM YIELD FOR 2-930 - 990 m $\mu$  VERSUS THE LOGARITHM OF THE FINAL THERMIONIC CURRENT AT THE END OF A BATH.



height of the infrared peak. It is interesting to note that the maximum sensitivity 6 and maximum infrared sensitivity curve 5 occur beyond the maxima in thermionic emission. The decay in the sensitivity with prolonged baking of the tube was linearly related to the logarithm of the thermionic current. It was rather surprising that the slope of the decay curve for thermionic emission and photosensitivity was approximately the same as for the growth curve. The point 11 in Fig. 32 corresponds to the maximum relative quantum yield difference at 920  $m\mu$  between curves 11 and 12, Fig. 29.

When cesium was returned to the tube at bake 13 there was no marked increase in the thermionic emission compared to the first series of bakes and the thermionic emission was not correlated with the photosensitivity characteristics of the tube.

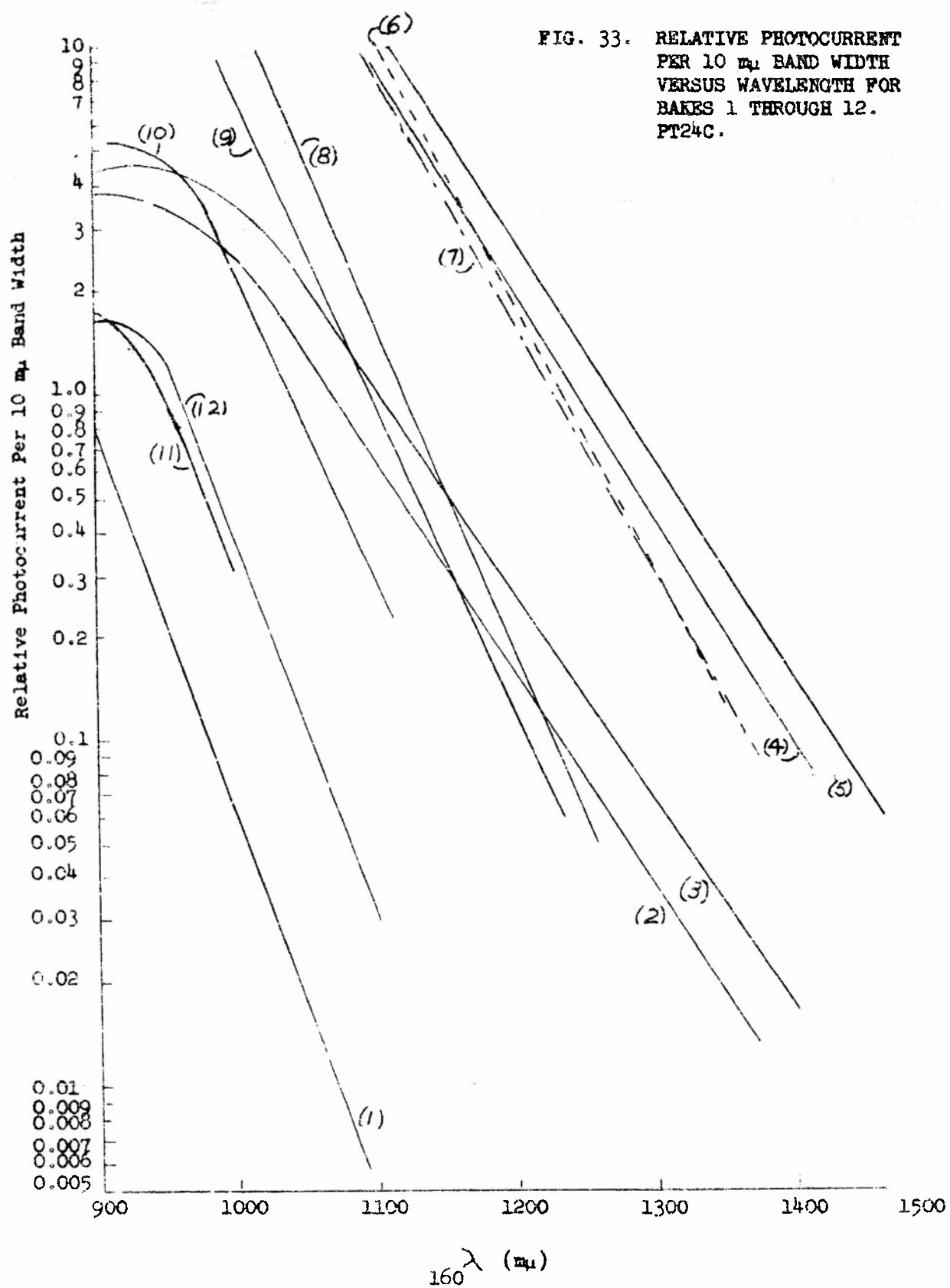
### 3.23 Long wavelength spectral yield

Since one factor of interest in describing the Ag-O-Cs photocathode is the behavior of the long wavelength region, a set of curves were prepared in which the logarithm of the dispersion corrected photocurrent was plotted versus the wavelength for  $\lambda > 900 m\mu$ . These data are shown in Figs. 33 and 34. It is apparent that these data may be approximately represented by an equation of the form:

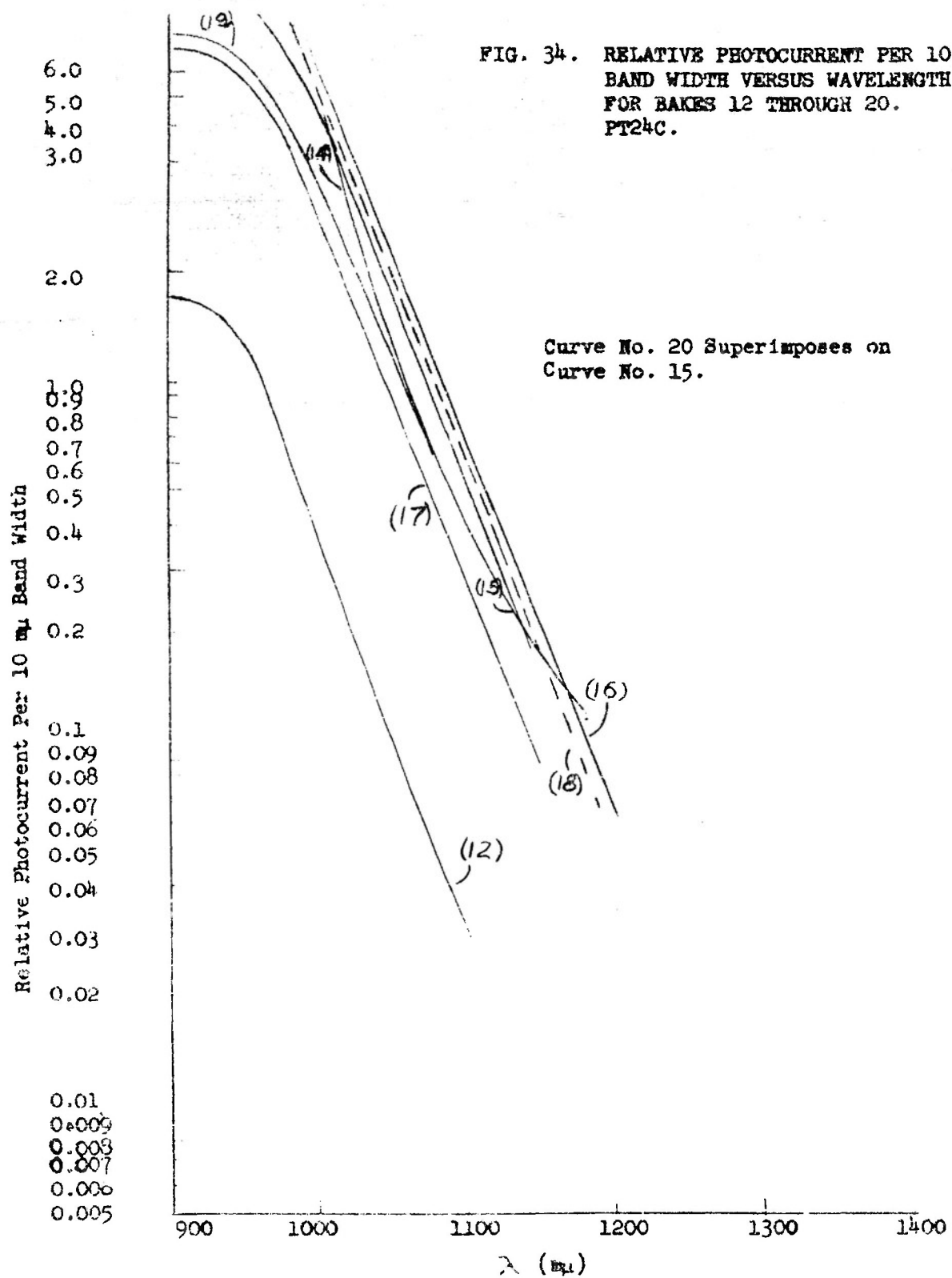
$$\log (i) = K_1 \lambda + K_2$$

where  $i$  is the photocurrent,  $\lambda$  the wavelength, and  $K_1$  and  $K_2$  are constants.

After the first bake the slope  $K_1$  was  $-0.0114$  per  $m\mu$ , decreasing after the second bake to  $-0.00630$  per  $m\mu$ , and remaining essentially constant through the fifth bake. The fifth bake corresponds to the maximum sensitivity in the infrared. After the sixth bake the infrared sensitivity began to decrease and for the bakes 6, 7, and 8 the slope  $K_1$  was  $-0.00771$ ,  $-0.00722$  and  $-0.00989$  per  $m\mu$  respectively. The slope after the ninth bake was relatively constant at  $-0.0114$  per  $m\mu$ . Thus, after bake 14 the slope is invariant and corresponds to that observed after the initial bake 1. The condition which produced the maximum sensitivity in the far infrared is not recovered on introducing more cesium into the tube and rebaking.







### 3.24 Development of infrared response

In the Beckman DU spectrophotometer the light source is an automotive type bulb (Mazda 2331) with a tungsten coil filament operated at 4.96 to 5.00 volts. The lamp color temperature as determined with a Leeds and Northrop pyrometer was approximately 2430°K. The temperature could not be well defined because of the different temperature existing within and outside the coil as well as cooling of the ends of the filament by the support. As a rough approximation the data given by Forsythe and Adams<sup>50</sup> for the spectral distribution from a 115-volt 25-watt vacuum lamp at a color temperature of 2530°K were used to correct the spectral sensitivity curves for the lamp energy distribution. By multiplying the photocurrent by the wavelength a relative quantum yield was obtained. To obtain an actual value of the quantum yield it would be necessary to know the energy actually absorbed by the surface as a function of the wavelength. The relative quantum yield as defined above is plotted as a function of the frequency as shown in Fig. 35 for bakes 1 through 6, and in Fig. 36 for bakes 6 through 12. It is interesting to note that correction for lamp energy distribution does not shift the position of the long wave maximum between 900 and 1000  $m\mu$  by very much. It is also of interest that the inflections previously noted become even more pronounced.

The form of the spectral sensitivity curves suggested an alternative way for considering the data. The assumption was made that the spectral curves for bakes 1 through 6 corresponded to a composite of two functions. The first function was obtained by forming the mirror image of the infrared portion of the spectral sensitivity curve about the ordinate corresponding to the maximum sensitivity. This set of curves for bakes 1 through 6 is shown in Fig. 37 and for bakes 6 through 11 in Fig. 38. Subtracting those curves from the corresponding spectral sensitivity curves results in the curves for the second function as shown by the primed numbers in Figs. 37 and 38. Thus by this procedure the development of photosensitivity may be described by two superimposed spectral distributions. It was rather surprising that reflection of the infrared portion of the curve about the maxima results in the formation of a family of curves which in the red portion of the spectrum have a common origin. In Fig. 38 curves 9 and 10 appear to fall outside the original family as defined by curves 1 through 6 in

FIG. 25. RELATIVE QUANTUM YIELD VERSUS  
FREQUENCY FOR BAKED  $\alpha$  THROUGH  
6. PT24C.

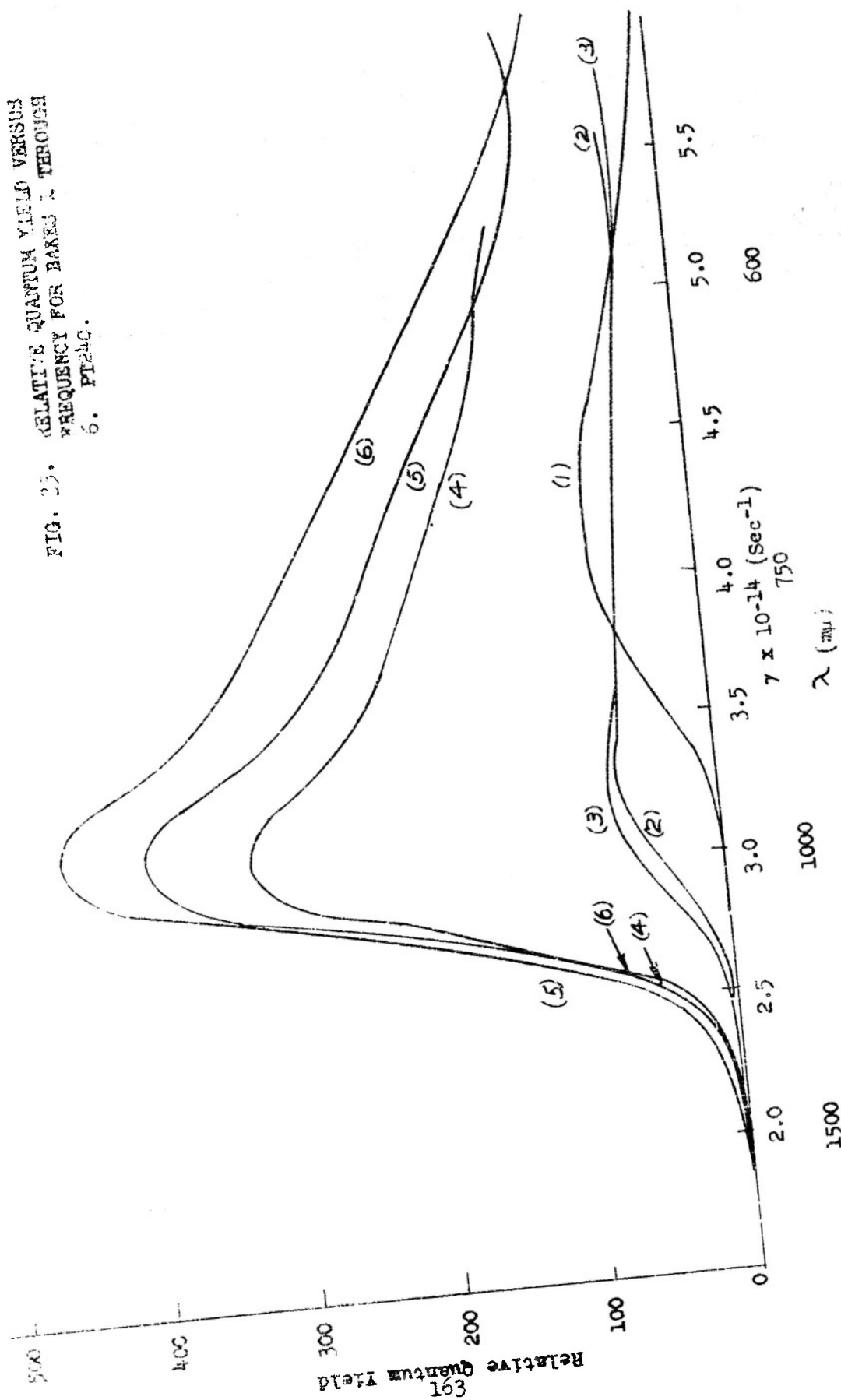


FIG. 35. RELATIVE QUANTUM YIELD  
VERSUS FREQUENCY FOR  
BAKE 5 THROUGH 12.  
PT24C.

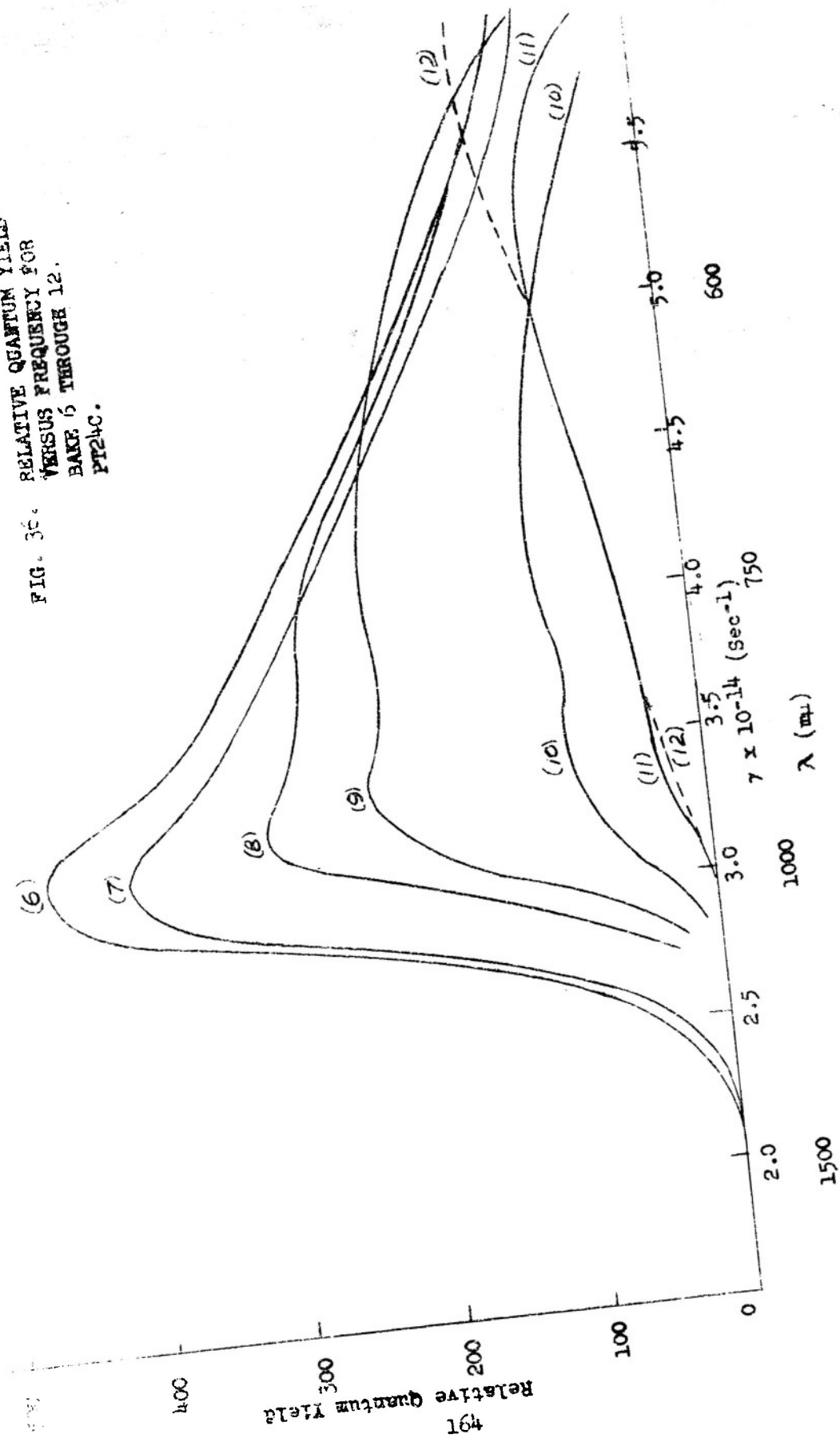


FIG. 37. RELATIVE QUANTUM YIELD VERSUS  
FREQUENCY CURVES DERIVED FROM  
FIG. 35 FOR BAKES 1 THROUGH 6;  
PT24C.

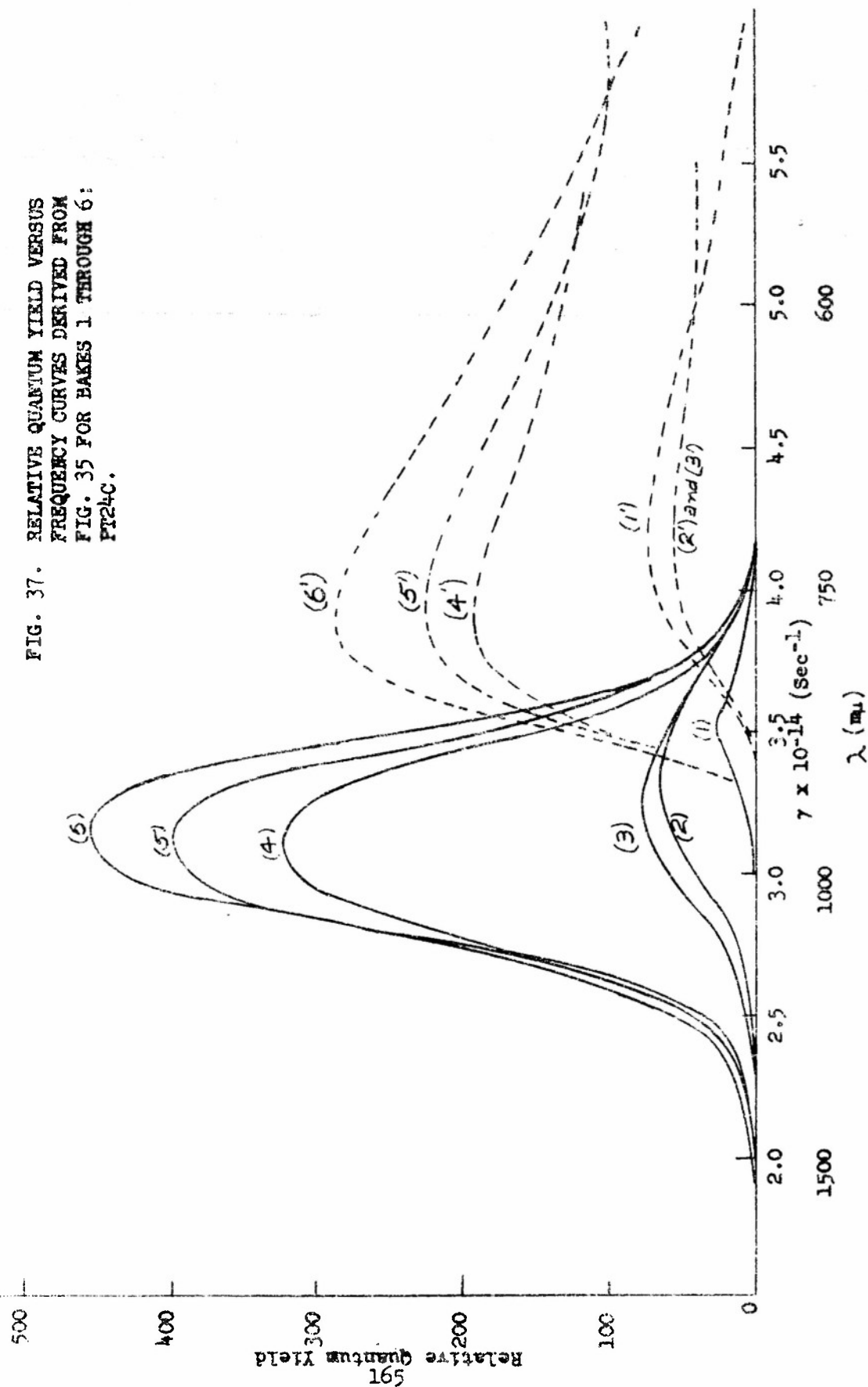


FIG. 38. RELATIVE QUANTUM YIELD VERSUS  
FREQUENCY CURVES DERIVED FROM  
FIG. 36 FOR BAKES 6 THROUGH 12.  
PT24C.

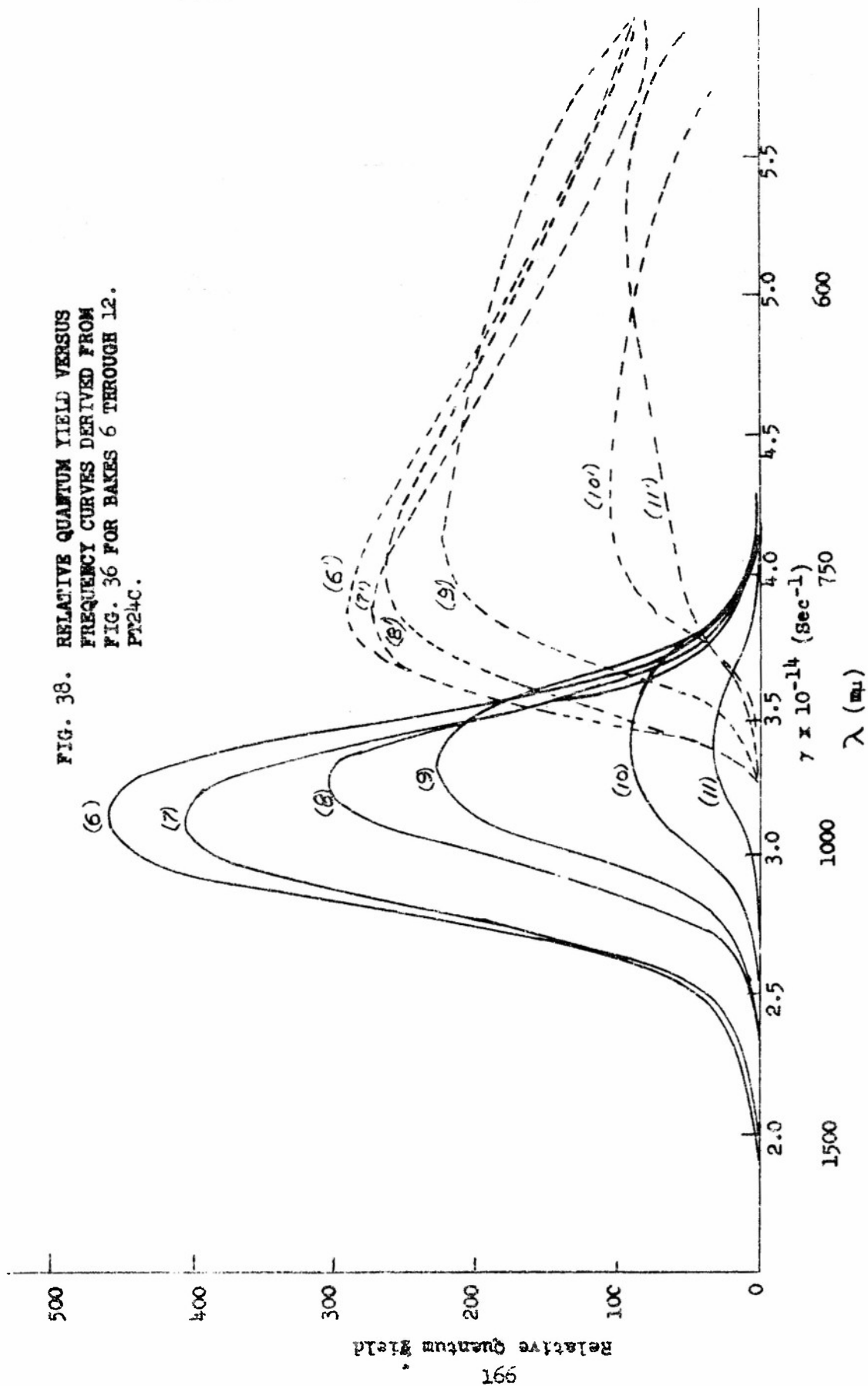


Fig. 37. If the assumption is made that in 9 a new phase for production of photoelectrons corresponding to curve 12 is being formed, then the data may be made more self consistent. The effect of applying such a correction to bake 9 data is shown in Fig. 39. When the spectral distribution is corrected for a 12 type of sensitivity and the resultant curve resolved into two functions, the infrared function belongs to the family defined in Fig. 37 for bakes 1 through 6.

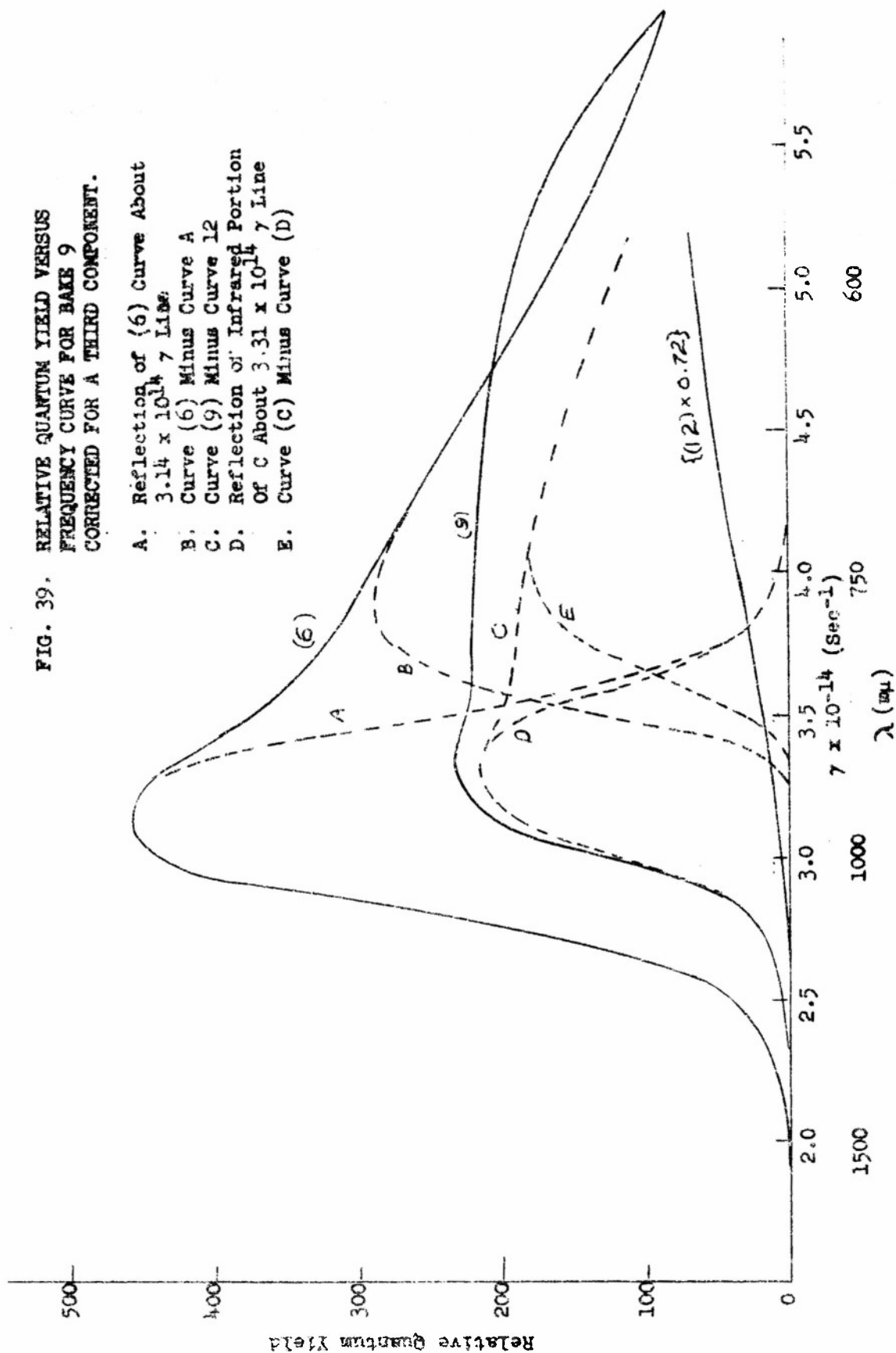
For the initial growth and decay in sensitivity with continued baking, the spectral distribution curves may be arbitrarily divided into three classes. The first type, Class I, corresponds to the development of a peak in the photosensitivity in the region of 900 - 1000  $m\mu$  with a spectral distribution function which resembles an error curve. In this case the long wavelength limit is related to the position of the maximum sensitivity but the visible spectrum limit of the curve remains essentially constant at 675  $m\mu$ . The second type, Class II, corresponds to the development of a maximum at 750 - 780  $m\mu$  with a long wavelength limit at approximately 910  $m\mu$ . The third type, Class III, corresponds to the linear increase in the photosensitivity with increasing frequency from a long wavelength limit of approximately 1150  $m\mu$ . This final curve corresponds to the limiting photosensitivity after extensive baking. The arbitrariness of this procedure is evident. There is no theoretical justification for the assumption that Class I curves are symmetrical and this assumption makes the long wave limit for Class II curves entirely untrustworthy. The implication of different emitting centers is, however, so strong that even this rough separation is worthwhile. The resemblance of the long wave maxima for Class II curves to those of Table IV Section 1.9 is very striking.

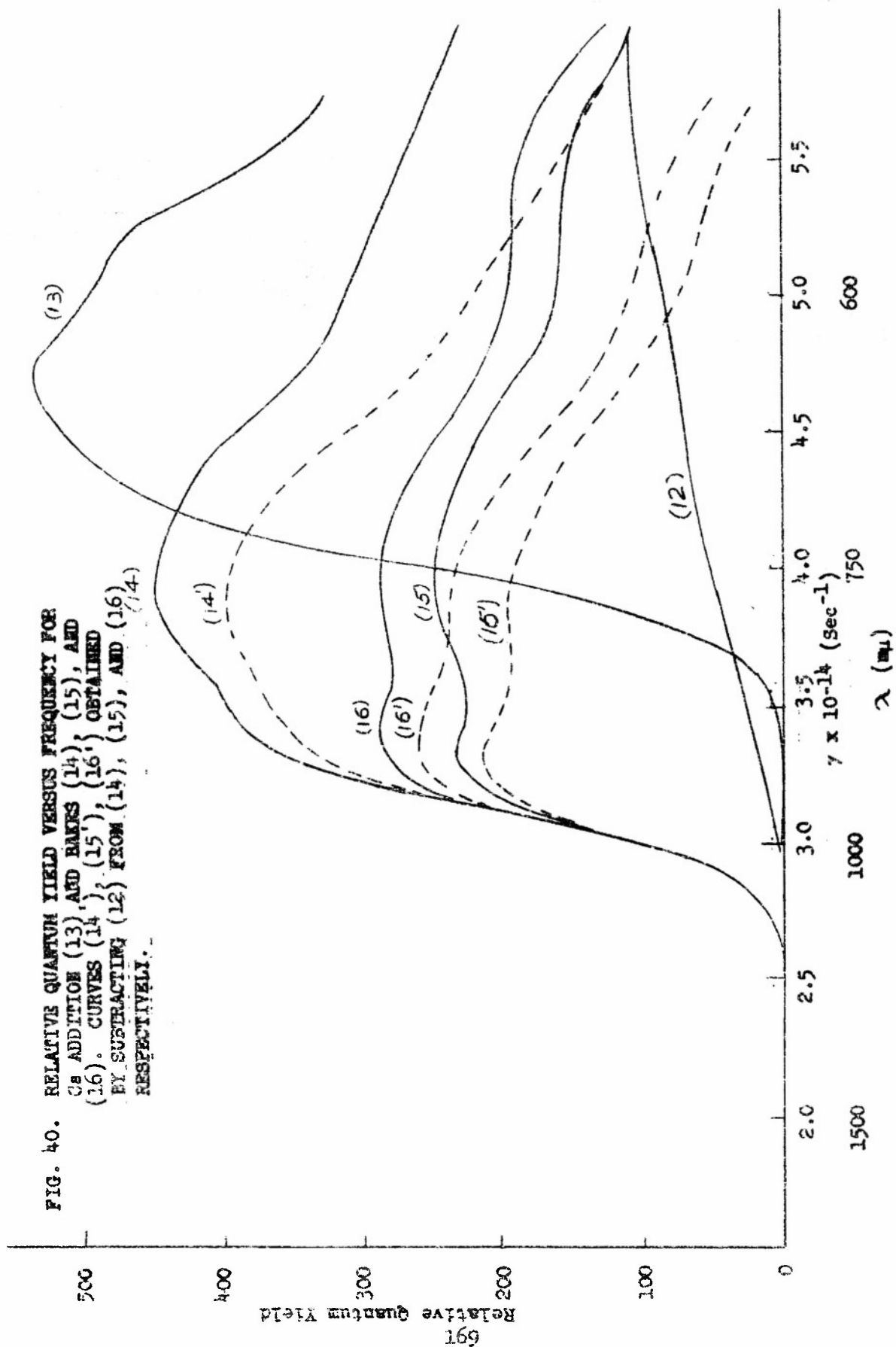
The variation in the relative quantum yield with frequency after the introduction of cesium at bake 13, and after bakes 14, 15, and 16 are shown in Fig. 40. The increase in emission in the visible portion of the spectrum with cesium addition is clearly shown in this figure. The spectral distribution for the tube at stage 13 resembles that presented by Zaitsev and Khlebnikov<sup>22</sup> for a thin-film Ag-O-Cs surface. The surface was prepared by repeated evaporation of Ag on the Ag-O-Cs surface and baking at 100-130°C in cesium vapor so that a surface is obtained which has its peak emission at approximately 590  $m\mu$  and a long wavelength limit at 1200  $m\mu$ .



FIG. 39. RELATIVE QUANTUM YIELD VERSUS  
FREQUENCY CURVE FOR BAKK 9  
CORRECTED FOR A THIRD COMPONENT.

- A. Reflection of (6) Curve About  
 $3.14 \times 10^{14} \gamma$  Line
- B. Curve (6) Minus Curve A
- C. Curve (9) Minus Curve 12
- D. Reflection of Infrared Portion  
Of C About  $3.31 \times 10^{14} \gamma$  Line
- E. Curve (C) Minus Curve (D)





For the spectral sensitivity curves of bakes, 14, 15, 16 the assumption was made that after the 14th bake a contribution of Class III corresponding to bake 12, Fig. 38, was present in the spectrum. The curves 14', 15', and 16', Fig. 40, were obtained by subtracting curve 12 from 14, 15, and 16 respectively. From these curves 14', 15', and 16' the curves shown in Fig. 41 for Class I and Class II spectral sensitivity contributions were derived. Comparison of the data for the 6th bake to that for the 14th bake, Fig. 41, shows that there was a decrease in the Class I sensitivity and an increase in the Class II sensitivity after the introduction of additional cesium and baking at 180 - 200°C.

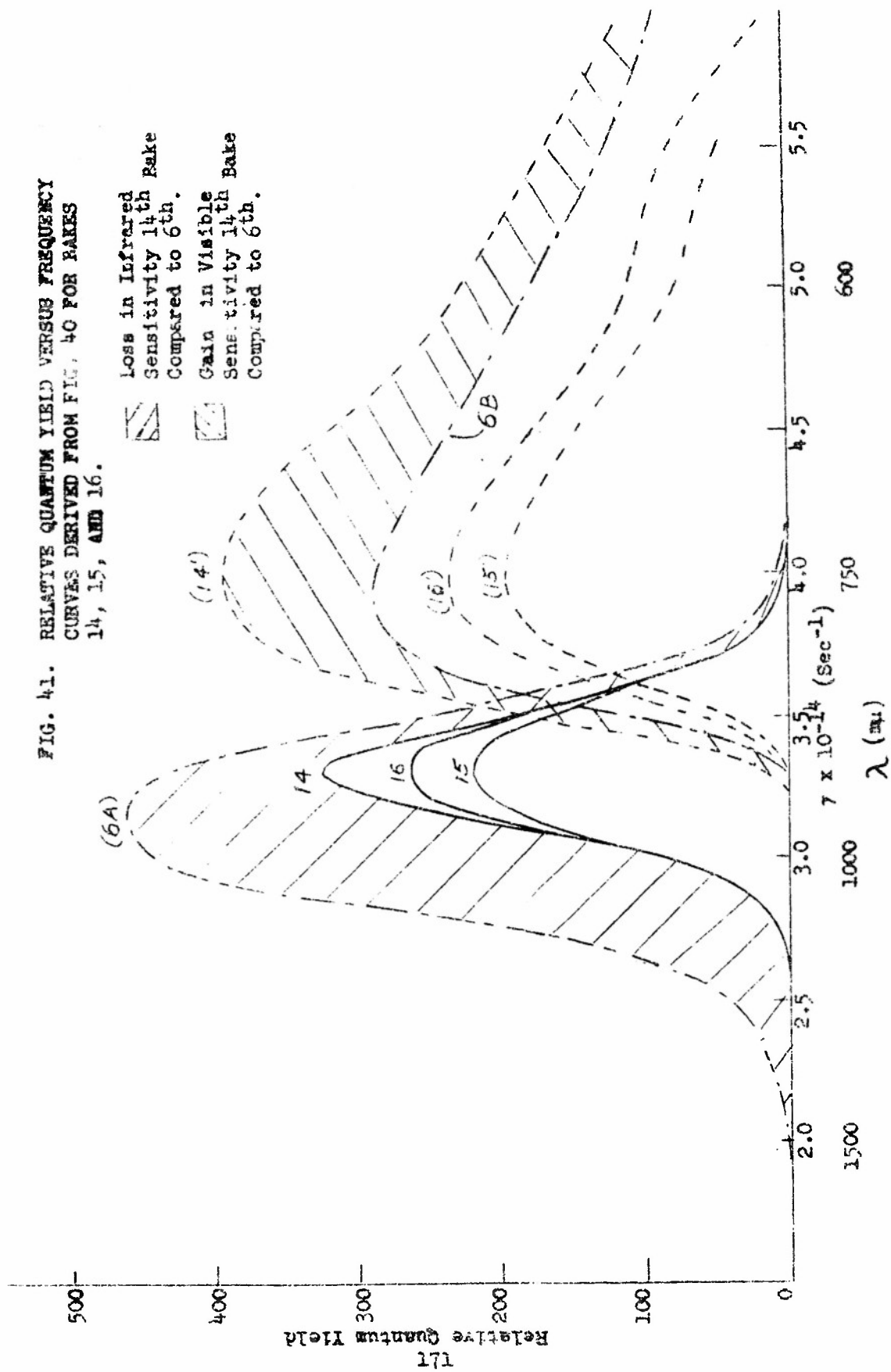
It has been stated that if the surface is baked to the ivory color and the spectral sensitivity has dropped to a low value, the white light sensitivity may be recovered by an argon glow discharge in the tube followed by re-evacuation (see ref. 14 p. 94). The spectral distribution for the recovered tube would have to be studied before any correlation with the results for PT24C may be made.

### 3.25 Discussion

The interpretation of the data for PT24C is complex because of the number of processes occurring simultaneously. In the first bake operation the excess cesium introduced no doubt reacts completely with silver oxide ( $\text{Ag}_2\text{O}$ ) to form ( $\text{Cs}_2\text{O}$ ) gross composition plus Ag, and a portion of the excess is distilled out of the tube. During the period of time when excess cesium is present there is also a transfer of oxygen away from the cathode (see Section 4.1). In addition, at 190°C the precipitated silver undergoes sintering and this probably influences the photoelectric response. At baking temperature cesium is also reacting with the pyrex glass tube envelope. Despite these complications several interesting points are established.

The expression of the spectral response curves as the sum of curves of three classes is obviously arbitrary. The suggestion of two different emitting centers contributing to the spectral response in roughly the manner indicated by Class I and Class II curves is, however, very strong indeed. This suggestion is not confined to the particular photocathode described here. Many examples have been observed, a number of which are described in subsequent sections. It has become possible to a considerable degree to control the proportions of Class I and Class II contributions and hence to understand the factors responsible

FIG. 41. RELATIVE QUANTUM YIELD VERSUS FREQUENCY  
CURVES DERIVED FROM FIG. 40 FOR BAKES  
14, 15, AND 16.



(see Section 3.4). We have, therefore, become convinced that the idea of at least two types of emitting centers is a valid one. We call attention again to the very close similarity of the Class II curves to the spectral responses obtained by the investigators listed in Table IV Section 1.9. Allowance must of course be made for the fact that the long wave limit for Class II curves is quite unreliable because of the arbitrary manner in which the Class I response is determined. This point will again be discussed in subsequent sections.

The suggestion of two types of emitting centers (I and II) arises from the appearance of the spectral response curves. These contain in some instances two maxima and in others a maximum and an inflection. The effect of the two types of centers is therefore pronounced and easy to recognize especially in comparing a series of related curves obtained at various stages of a baking operation. It is evident from inspecting the response curves that centers of both types are contributing simultaneously to the same cathode. That centers of a third type, contributing in a manner indicated by Class III curves, are also contributing to the same cathodes is not well established. It is not easy to detect a contribution from type III centers by merely inspecting the spectral response curves and, on the whole, the basis for this hypothesis is weak. The previous analysis implies that centers of type III are produced on extended baking and, once produced, are not completely removed on reintroducing cesium. That such centers exist is, of course, suggested by the fact that curve 12 of Fig. 36 cannot be classified as either Class I or II or any combination of the two. Since, however, a contribution of type III to other curves than 12 is not clearly marked in the response curves, we cannot consider that this idea is firmly established. In Section 4.32 the types of spectral responses obtained under various conditions of preparation are summarized. The classification given there extends that discussed above.

That centers of two types, and perhaps a third, contribute to the spectral yield is strongly suggested by the data. When, however, we come to consideration of the chemical changes which accompany the alteration in spectral response on baking, the interpretation is complicated by a number of factors. In the first paragraph of this section it was implied that cesium reacts completely with silver oxide to form a mixture of cesium oxides. It was the intention in performing the experiment to produce an initial (Cs/O) ratio greater than 2 in the photocathode. At the time we did not realize how slow the cathode reactions actually are and hence in the first bake it is quite possible

that the bulk of the cesium distilled into the cold trap leaving a (Cs/O) ratio for the cathode which exceeds 2 by little if any. If the ratio did exceed 2 then the subsequent baking would undoubtedly produce  $\text{Cs}_2\text{O}$  in the cathode which contains little if any excess cesium. We cannot be sure, however, that the ratio of the number of cesium atoms to the number of oxygen atoms in chemical combination actually did exceed 2 and hence the data do not justify the conclusion that  $\text{Cs}_2\text{O}$  (mixed with silver) constitutes the photoelectric emitter. This point has been tested in a more clear-cut way with another massive cathode discussed in Section 3.32. The results of this subsequent experiment coupled with the results of Section 3.1 and the x-ray study of Section 4.2 make it virtually certain that  $\text{Cs}_2\text{O}$  (mixed with silver) is the infrared emitter. Despite the fact that the data on PT24C do not provide a clear-cut demonstration that  $\text{Cs}_2\text{O}$  (mixed with silver) is the photoelectric emitter another important point is established. After having removed infrared by baking it is found that sensitivity can be partially restored by permitting cesium to distill back from the trap to the cathode. This immediately suggests that loss of sensitivity on extended baking is due to loss of cesium. This view also agrees with the results of Section 3.1 which indicate an optimum cesium content at which infrared sensitivity is a maximum. It must be noted, however, that the cathode sensitivity is not an accurately reversible function of cesium content since infrared sensitivity is not recovered when cesium is distilled back into the cathode. None of the spectral responses of Fig. 40 extend as far into the infrared as does curve 6 of Fig. 35. Moreover, the thermionic emission never rises to as high a value, after distilling cesium back to the cathode, as was previously attained. These observations establish, therefore, that distillation of cesium away from the cathode is not the only change which accompanies extended baking. Other, permanent, changes have also taken place. This is hardly surprising. It is obvious that extended baking at  $190^\circ\text{C}$  will lead to grain growth of both the cesium oxides and precipitated silver. If, moreover, the (Cs/O) ratio for the cathode were initially greater than 2 then baking would result in the formation of a volatile cesium oxide (see Section 4.1) and hence oxygen is also transported away from the cathode. In view of these facts the observation that reversibility of infrared sensitivity is incomplete does not seem surprising.

### 3.3 Distillation Technique for Preparing Cs<sub>2</sub>O

The work of Campbell<sup>20</sup>, Prescott and Kelly<sup>18</sup> and Sayama<sup>21</sup> indicate that Cs<sub>2</sub>O is an essential ingredient in a highly infrared-sensitive silver-oxygen-cesium photocathode. It seemed logical to suppose, therefore, that a cathode prepared in such a way as to contain Cs<sub>2</sub>O would be infrared-sensitive. In order to test this idea several cathodes were therefore prepared by methods which differ from those commonly used but which were of such a nature as to produce Cs<sub>2</sub>O as the final product. The preparation is based on the fact that on heating (at 190°C) a suboxide of cesium for which (Cs/O) > 2 cesium can be distilled out and the final solid is Cs<sub>2</sub>O. It must be emphasized that it is a proven fact that Cs<sub>2</sub>O is the final product of such a process. The Cs<sub>2</sub>O samples used in the crystal structure determination of Part III of this Final Report Series were prepared in this way and the identity of the product established conclusively. The amount of impurity does not exceed 0.1 mole percent. Photocathode PT24C of the preceding section was prepared for the purpose of testing the above idea but the test was not conclusive because, as stated in the previous section, we could not be sure that the cesium introduced had reacted with silver oxide sufficiently to make the ratio of combined cesium to oxygen atoms greater than 2 before the cathode was heated to 190°C and the distillation begun. In this section the results obtained with two additional cathodes, PT26 and PT35C, are described. In the case of PT35C there is no doubt that the (Cs/O) ratio exceeded 2 before distillation begun. In the case of PT26, a semitransparent cathode, the same questions arise as in the case of PT24C. The infrared sensitivity of PT26 also turned out to be low. We now know, however, that this is due to the thin silver base used in the preparation rather than to any failure to produce Cs<sub>2</sub>O in the cathode. The results are, therefore, included since they illustrate an important point although not in quite the way that was anticipated before the experiment was performed.

#### 3.31 Semitransparent cathodes

The semitransparent cathode PT26, described below, was prepared in such a way as to contain Cs<sub>2</sub>O by first adding excess cesium to the tube and then, at 190°C, distilling out some of the excess into an attached cold trap. Several other semitransparent cathodes were prepared in a similar way, and also by other methods. The



results obtained for PT26 are typical of the whole group.

In the fabrication of PT26 the tube was first heated at 300°C until the final pressure became  $2 \times 10^{-6}$  mm Hg. After evaporating a 25% transmission silver film, the surface was oxidized by means of an rf glow discharge to 60% transmission. This process, as was later shown (see Part I), corresponded to complete oxidation of the silver. A second silver layer was then deposited to give a final transmission of 37%. The tube was then evacuated, the  $\text{Cs}_2\text{CrO}_4$ -Si pellet fired, and the tube tipped off the vacuum system. The dry ice-acetone trap, which was sealed to the tube, was cooled and the tube baked in a manner similar to PT24, but at successively higher temperatures starting at 120°C. The baking data for PT26 are summarized in Table X.

The tube PT26 did not develop appreciable sensitivity in the infrared portion of the spectrum as shown in Fig. 42. After the first bake the spectral distribution maximum was at 595  $m\mu$  and the long  $\lambda$  limit at 800  $m\mu$ . After the fourth bake the maximum had shifted to 710  $m\mu$  and the long wavelength limit to 1000  $m\mu$ . Following the fourth bake the sensitivity steadily decreased in the manner shown by curves 5 and 6 in Fig. 42. The cathode actually had a very low sensitivity as shown in Fig. 43 where the relative quantum yields are drawn to the same scale as those for PT24C described in the previous section. It is interesting to note that the form of curves 2, 3, and 4 are similar to the Class II curves obtained for PT24C after deducting the Class I infrared response curves, while curve 6 is similar to the curve obtained after PT24C had been given an extended bake to destroy the infrared sensitivity. The introduction of cesium from the trap followed by further baking resulted in a further decrease in the sensitivity. During the processing, as indicated in Table X, there appeared to be an increase in the thermionic emission. It is rather doubtful that the recorded current is due to thermionic emission. It seems probable that an ohmic conduction current along the tube envelope is involved.

After a number of similar experiments, using a variety of baking conditions, it was concluded that a good infrared semitransparent cathode could not be readily formed using a distillation technique for producing  $\text{Cs}_2\text{O}$ . This originally raised the question of whether or not  $\text{Cs}_2\text{O}$  was the photo-emitter. Later experiments, however, demonstrated that such a distillation technique is a rather complex process involving among other phenomena a transport of a cesium oxide in the vapor phase when excess cesium is present (see Section 4.1).

TABLE I. BAKING DATA FOR SEMITRANSSPARENT CATHODE PT26

Bake No.	Bake Cycle	Time to Temp.	Time at Temp.	Thermionic Current ( $\mu$ a)	Long $\lambda$ Limit	Spectral Data
1	heat to 120°C	17 min	0	0.000	800	curve 1 Fig. 20
2	heat to 140°C	24	0	0.030	900	curve 2 Fig. 20
3	heat to 150°C	21	0	0.036	925	curve 3 Fig. 20
4	heat to 180°C	20	0	0.144	1000	curve 4 Fig. 20
5	heat to 190°C	2	0	0.348	1050	curve 5 Fig. 20
6(1)	heat to 180°C	9	4	0.090	1050	curve 6 Fig. 20
7(2)	warm trap, add Cs and heat to 190°C - 200°C	10				peak 570 m $\mu$
8	heat to 165°C	60	15	0.060	-	peak 570 m $\mu$
9	heat to 190°C			0.036	-	peak 570 m $\mu$
10	bake entire tube at 130°C, cool trap and bake at 200°C		30			peak 490 m $\mu$

(1) From bake 6 through 10 the spectral sensitivity continually decreased.

(2) Only for bakes 7 and 10 was the trap removed from the dry ice-acetone mixture.

FIG. 42. SPECTRAL RESPONSE PT26.

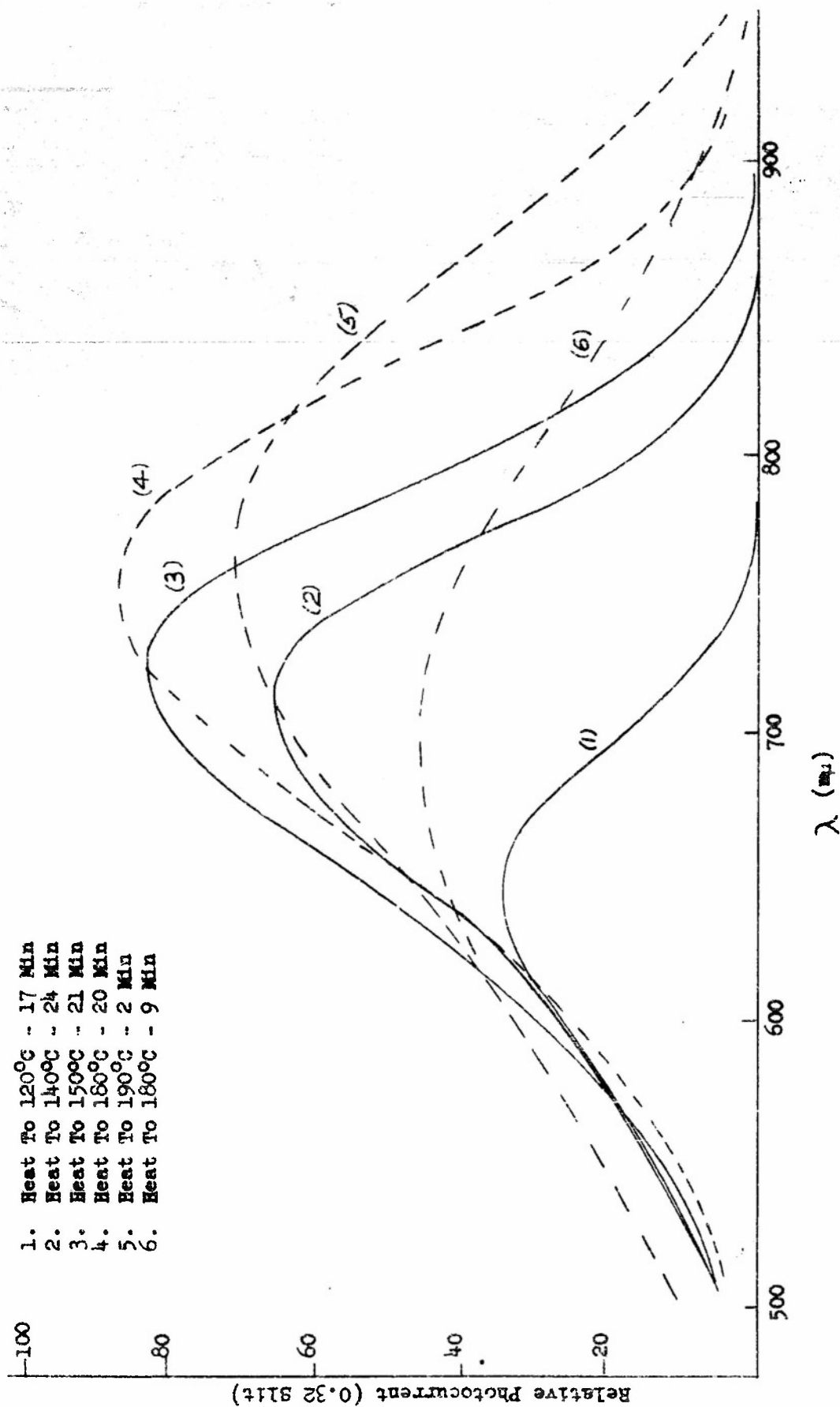
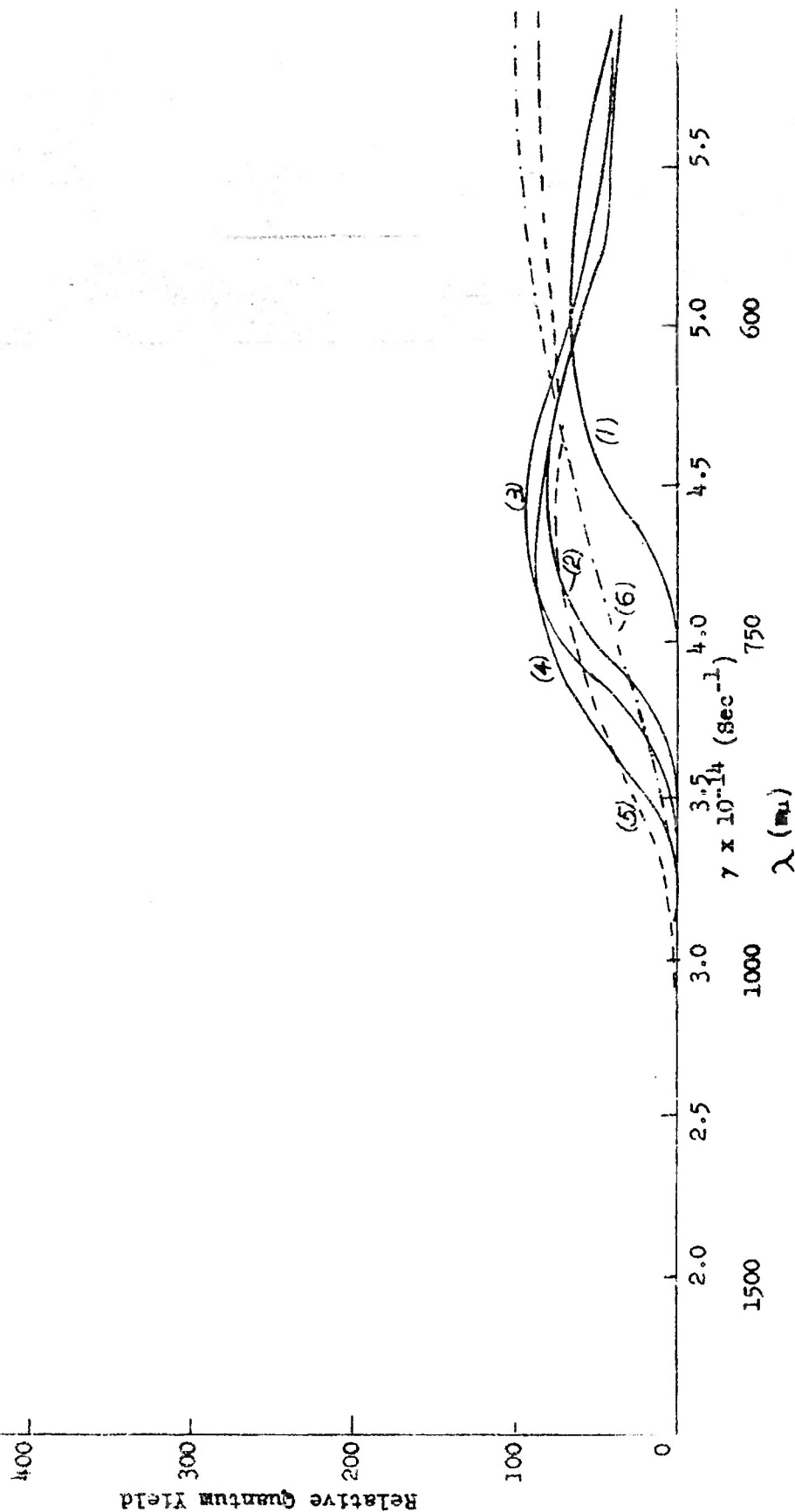


FIG. 43. RELATIVE QUANTUM YIELD VERSUS FREQUENCY FOR PT-26.  
COMPARABLE DIRECTLY TO SIMILAR CURVES FOR PT24C -  
SECTION 3.2.



This factor may account in part for the low infrared sensitivity compared to that obtained for massive cathodes such as PT24C of the previous section. In view, however, of the pronounced effect of silver base which was later discovered (see Section 3.51) it now seems likely that the distribution of silver in the cathode is responsible for the low infrared sensitivity. Since, as discussed in Section 1, both silver and  $\text{Cs}_2\text{O}$  are probably involved in producing infrared sensitivity this is probably not surprising. The result obtained was, however, unexpected at the time the experiments were performed.

In speaking of PT26 as having a low infrared sensitivity we are thinking in terms of comparing the tube with good massive cathodes such as PT24C or with commercial semitransparent cathodes such as the PT25 tube of Fig. 9. When, however, we compare the shape of the spectral response curves for PT26 with some of those given by the investigators listed in Table IV of Section 1 we see that there is not much difference. In particular the shapes of the spectral response curves of Fig. 43 are rather similar to those obtained by Morozov and Butslov<sup>24</sup> in the study of wedge type photocathodes. This fact is further discussed in a later section.

### 3.32 Massive cathodes

As a result of the difficulties encountered in preparing infrared-sensitive semitransparent cathodes by a distillation technique it was desirable to establish whether or not a similar behavior occurred in the preparation of massive cathodes. To illustrate the process for massive cathodes the data for tube PT35 are used.

Tube PT35 was a massive cathode tube similar in design to the tubes used in the composition studies previously discussed in Section 3.1. Unlike the tubes of Section 3.1, however, cesium was added to the tube while it was still attached to the vacuum manifold using a galvanometer to measure the thermionic emission during cesium addition. The cesium flow rate was controlled by means of a 2.5 cm section of 2 mm bore capillary connecting the combination cesium source and trap to the tube. The flow rate is therefore considerably larger than those of Section 3.1. After introducing excess cesium into the tube, the side tube section was cooled with a dry ice-acetone mixture. The fabrication data for PT35 are given in Table XI.

TABLE XI. FABRICATION DATA PT35 MASSIVE CATHODE

Tube	Operation	Moles O <sub>2</sub> / Sq. cm x 10 <sup>7</sup>	Oxide Color	Furnace Cs Source	Temp. Tube °C	Time min	Wavelengths (mμ)		
							Long Limit	Max. Sens.	Max. Sens.
PT35C	Fab.	2.41	1st blue	135	190	-	775	650	695
	Bake 1				135	120	1070	750	855
	Bake 2				135	150	1160	775	905
	16 hrs. 25°C trap at 25°C						900	680	740
	Bake 3			{ +	130	30			
					160	176	1350	890	985
	Bake 4				168	86	1350	890	1000
	7 days 25°C trap at 25°C						850	640	705
	Bake 5		Tube and trap baked at 100°C for 150 minutes 120 μa leakage current at 185 volts.						
	Bake 6				170	210	1200	790	925
	Bake 7				170	175	1250	875	970

The results obtained with PT35 may be conveniently described in terms of the thermionic emission and spectral response curves. The results are as follows:

1. During fabrication, cesium was introduced beyond the maximum thermionic emission as shown in Fig. 44. Although the tube was attached to the vacuum manifold during cesium addition there can be no doubt from the appearance of Fig. 44, taken in conjunction with the results of Section 3.1, that a (Cs/O) ratio greater than 2 was attained. After sealing the tube off the vacuum system the spectral response under standard conditions had a maximum at 650  $m\mu$  and a long wavelength limit of 775  $m\mu$  (curve 1 Fig. 46).
2. Baking the cathode at 1350°C for 120 minutes to distill excess Cs into the trap did not result in the development of thermionic emission but the response maximum shifted from 650 to 750  $m\mu$  and the long wavelength limit from 775 to 1070  $m\mu$  (curve 2 Fig. 46).
3. After rebaking at 1350°C for 150 minutes no thermionic emission appeared but the photocurrent maximum shifted from 750 to 775  $m\mu$  and the long wavelength limit from 1070 to 1160  $m\mu$  (curve 3 Fig. 46).
4. After the tube and trap had been at room temperature for 16 hours the response was remeasured. The peak and long wavelength limit had shifted back to 680 and 900  $m\mu$  respectively (curve 4 Fig. 46). The loss in sensitivity is due to the accumulation of a thin film of cesium on the cathode at room temperature (see Section 3.41).
5. After rebaking at 1300°C for 30 minutes without developing appreciable thermionic emission, the oven temperature was raised to 1600°C. The tube was then baked to constant thermionic emission at 1600°C as shown by the bake 3 curve of Fig. 45. The tube developed appreciable infrared sensitivity as shown by curve 5 Fig. 46. Peak and long wavelength limits were 890 and 1350  $m\mu$  respectively. Note the inflection near 750  $m\mu$ .



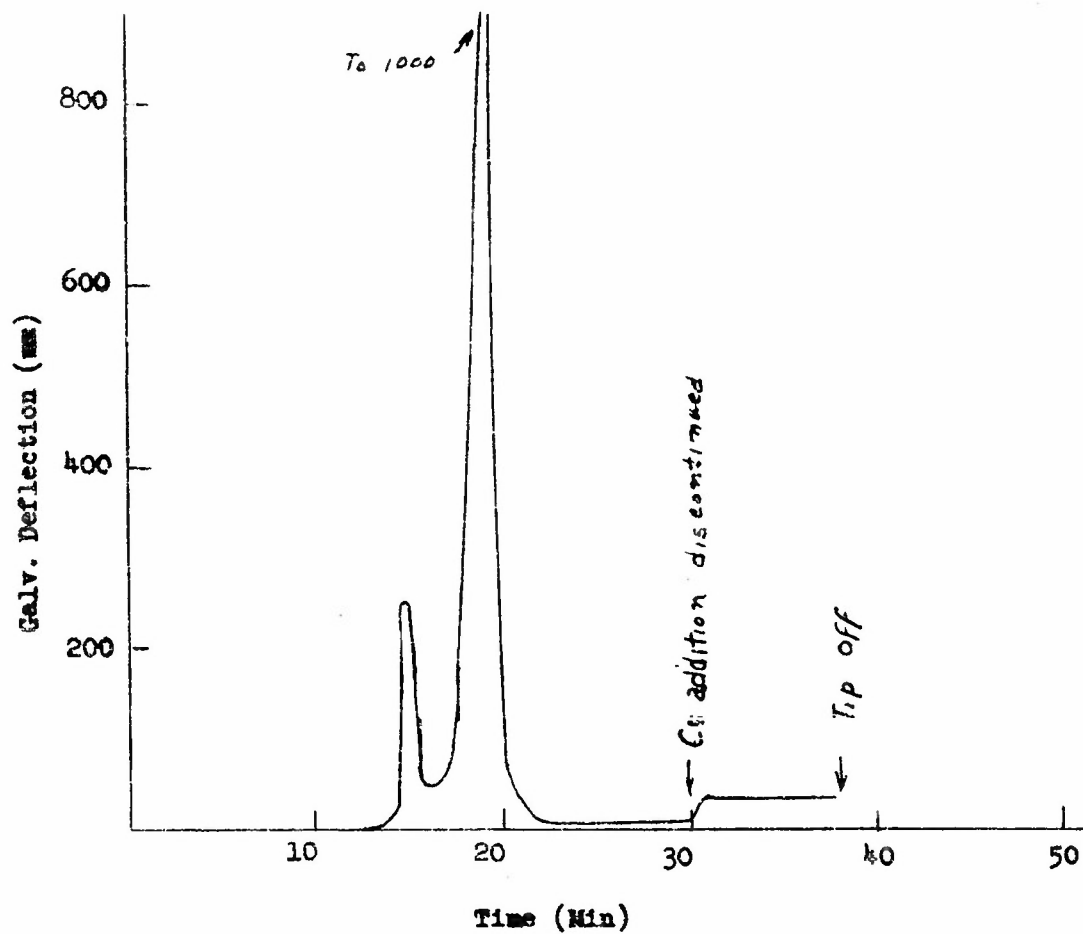


FIG. 44. THERMIONIC EMISSION PT35C INITIAL CESIUM ADDITION

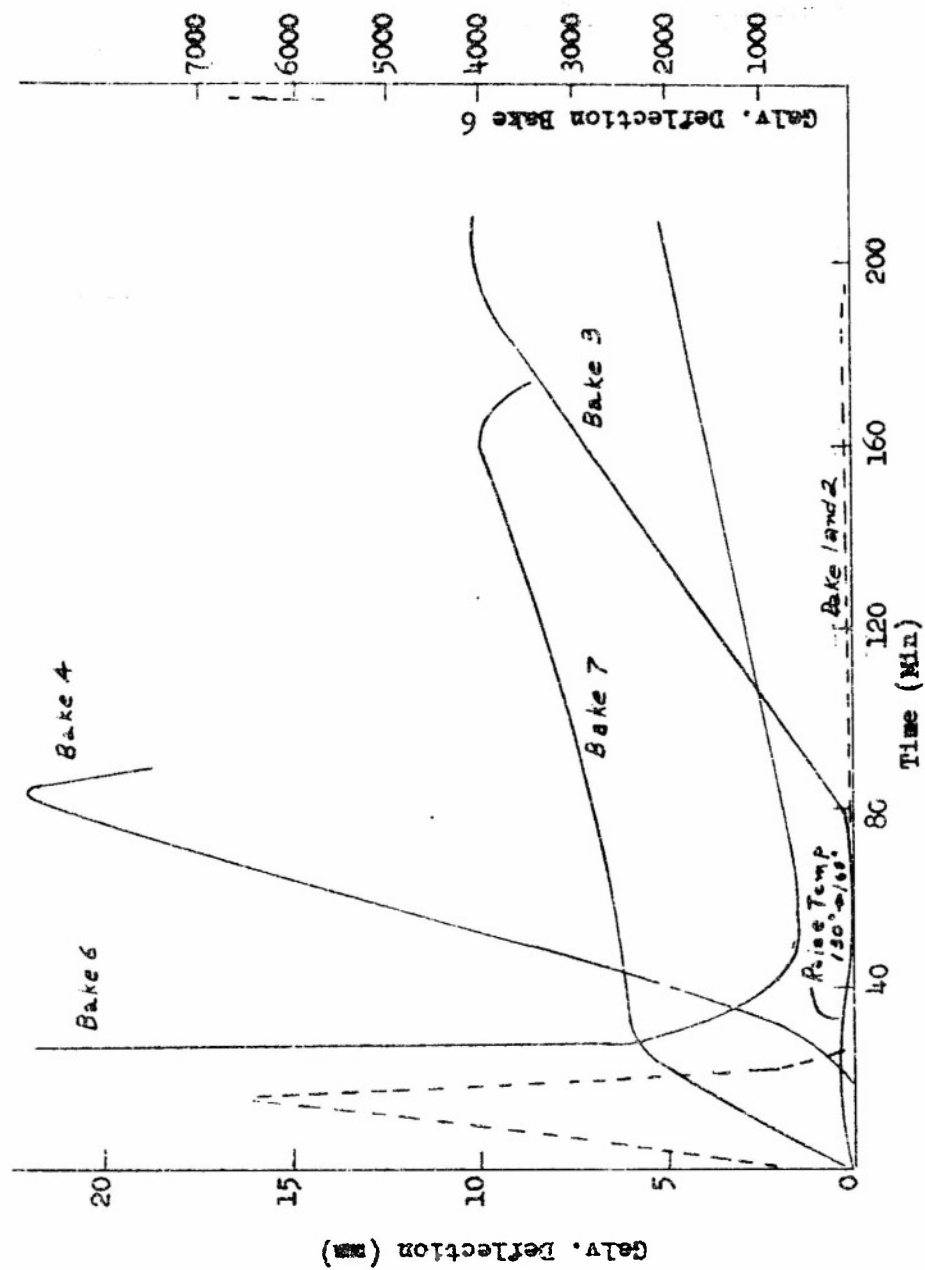
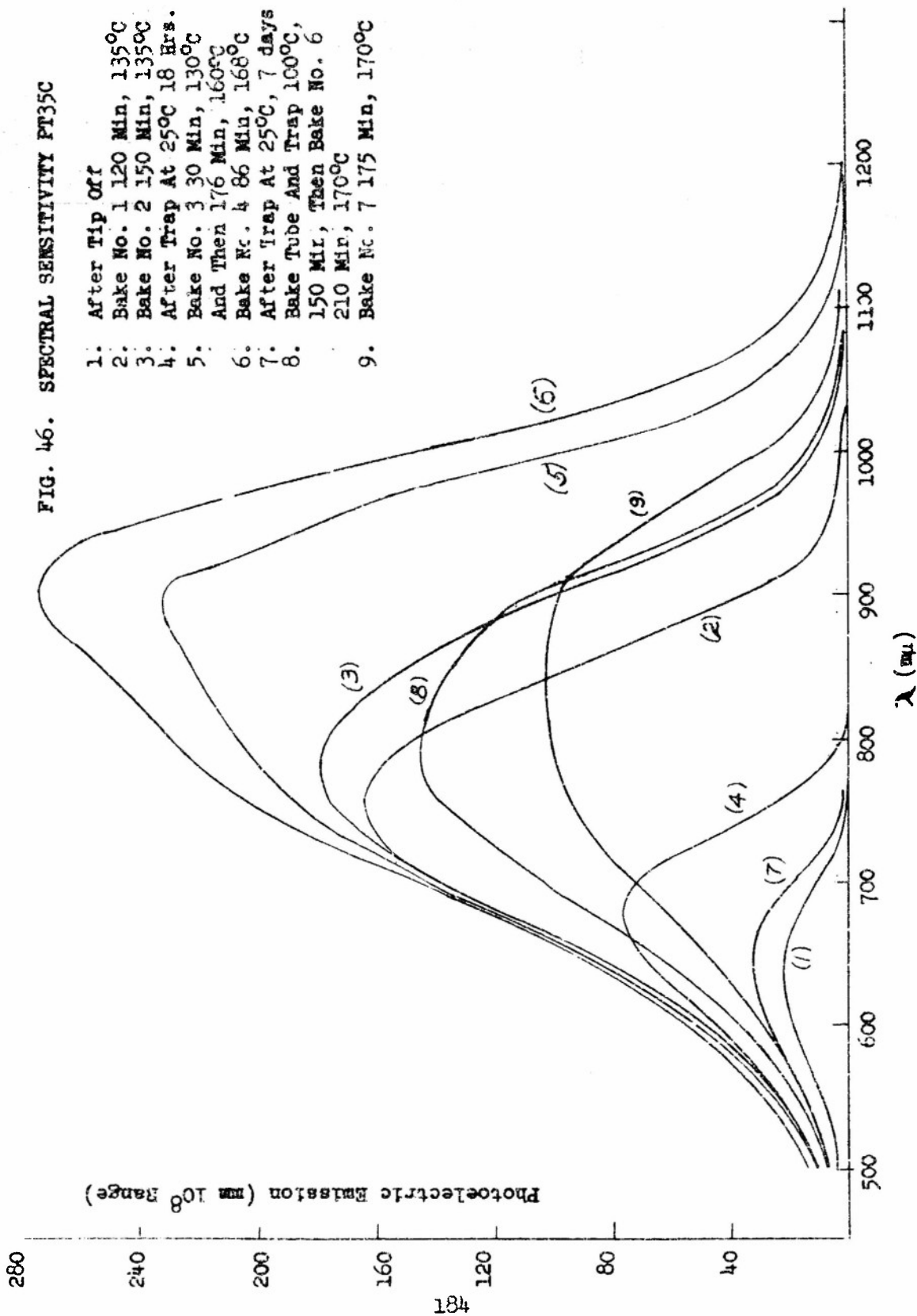


FIG. 45. THERMIONIC EMISSION PT35C DURING BAKING.

- Bake No. 1 - 120 Min, 135°C
- No. 2 - 150 Min, 135°C
- No. 3 - 30 Min, 130°C and Then 176 Min, 160°C
- No. 4 - 86 Min, 168°C
- No. 6 - Bake Tube and Trap 100°C, 150 Min And Then Bake No. 6  
210 Min, 170°C
- No. 7 - 175 Min, 170°C



6. The tube was rebaked at 169°C beyond a maximum in thermionic emission as shown by the bake 4 curve in Fig. 45. There was an increase in the photoemission but the peak wavelength and the long wavelength limit did not change.
7. After the trap and tube were at room temperature for 7 days the spectral response curve (7 Fig. 46) was similar to that after tip off and operation 4 above (see Section 3.11).
8. To equilibrate the surface with excess cesium the tube and trap were baked at 100°C for 150 minutes. After this bake, the leakage current was too large to determine the spectral response.
9. The tube was baked for 210 minutes at 170°C to distill the excess cesium into the trap. The dotted curve in Fig. 45 corresponds to the leakage current through the tube produced by the excess cesium on the tube walls. The baking was continued until the thermionic emission became stabilized. The spectral response had a maximum at 790  $m\mu$  and a long  $\lambda$  limit of 1200  $m\mu$ .
10. The tube was rebaked at 170°C until the thermionic emission passed a maximum as shown by the bake 7 curve Fig. 45. The spectral sensitivity of the cathode decreased but the maximum shifted from 790 to 875  $m\mu$  and the long  $\lambda$  limit from 1200 to 1250  $m\mu$ .

The first observation on the data for PT35C concerns the hypothesis of two types of emitting centers for massive cathodes which was advanced in Section 3.2. Curves 5 and 6 of Fig. 46 again strongly suggest that two types of centers are contributing to photoelectric emission. It must be noted, however, that maximum photoelectric yield is obtained at about 900  $m\mu$  in curves 5 and 6 of Fig. 46. Whereas the maximum obtained in bake 6 on PT24C (see Table IX) lies at 980  $m\mu$ . The trend shown in Fig. 46 suggests that further baking of PT35C, perhaps at higher temperatures, would move the maximum further into the infrared. It is found, however, that once a photocathode has been exposed to a large excess of cesium it is not easy to attain the high infrared sensitivity characteristic of the "normal" massive cathodes discussed in Section 3.13. In some experiments on other massive cathodes, which had been exposed to large excesses of cesium, it was necessary to heat the tube envelope with a hand torch in order to achieve the

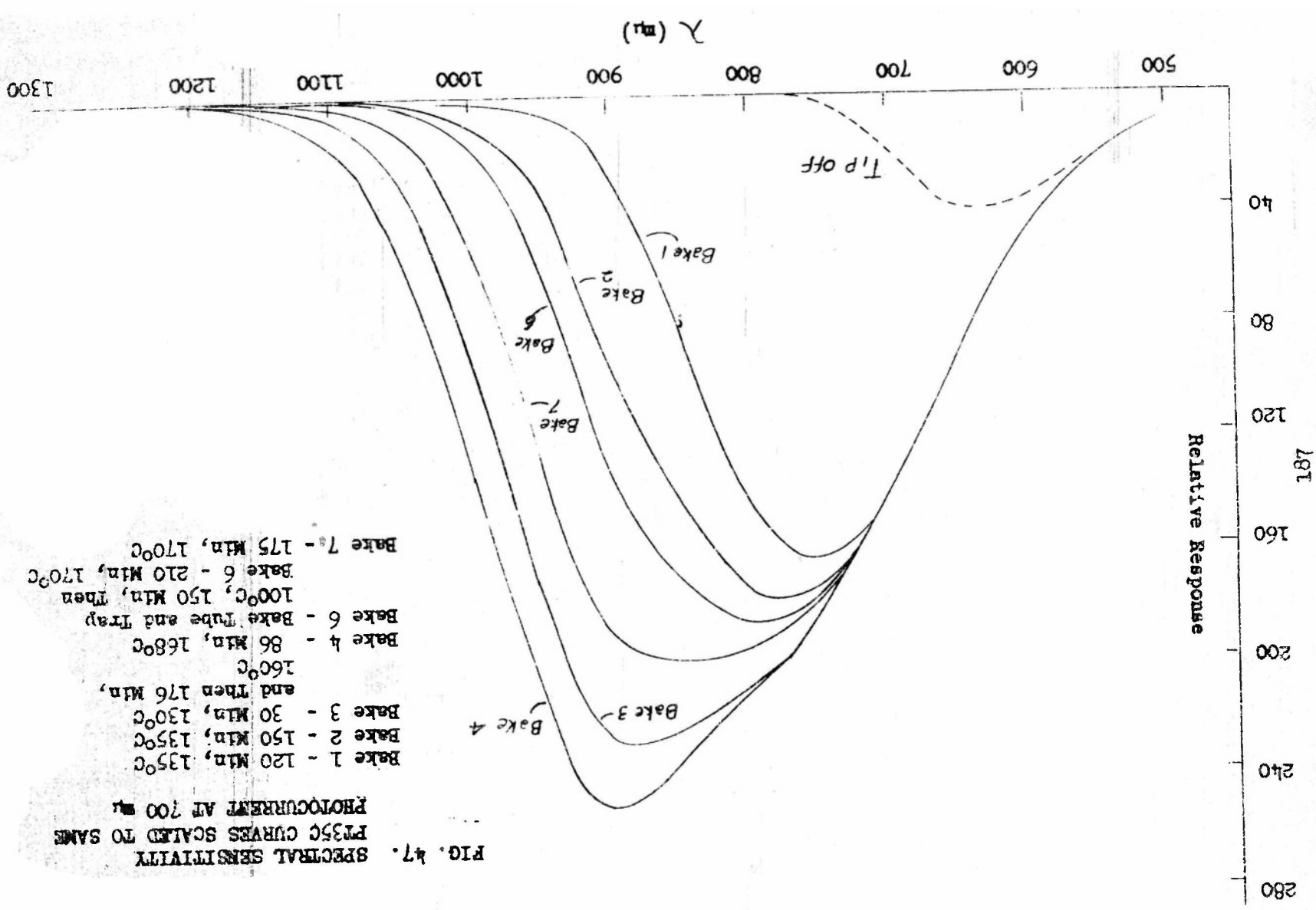
sensitivity characteristic of "normal" massive cathodes. This presumably resulted in speeding up the reaction of cesium with the glass envelope of the tube. No such drastic measures were used on PT35C.

Further analysis of the data on PT35C is useful in order to make comparison with PT24C, Section 3.2, easier. This is expedited by the following observation. The similarity of the spectral response curves, after baking, of Fig. 46 at wavelengths below 700 m $\mu$  suggests that the curves differ, below this wavelength, by a scale factor. Hence, in order to simplify the comparison, the set of spectral response curves in Fig. 47 were prepared by scaling the responses to the same 700 m $\mu$  photocurrent. The set form a well defined family and illustrate the development of photoemission in a cathode by removing excess cesium from the surface.

Comparison of the family of curves in Fig. 47 to those for PT24C (Fig. 28) indicates an interesting difference. Curves 1, 2, 3 of Fig. 28 resemble curves 2, 3, 5, 6 of Fig. 46 in that infrared response at wavelengths greater than 700 m $\mu$  is increasing while at smaller wavelengths the response changes but little on baking. Curves 4, 5, 6 of Fig. 28 show, however, that on further baking of PT24C growth in response is taking place over the entire wavelength range. From Fig. 47 it appears that the growth of photoemission for PT35C occurs by a process in which infrared emission is added to a characteristic emission already present. The reason for the difference is not fully understood. However, see Section 3.41 for a set of spectral curves obtained on adding cesium.

Using the spectral response curve for bake 1 as a reference curve, the family of difference curves for the growth of infrared sensitivity shown in Fig. 48 were computed. The growth of infrared sensitivity is qualitatively similar to the development of photoemission in PT24C but differs in detail, as discussed above. As shown in the following section (3.4) the choice of the bake 1 curve as a response base is not on an entirely arbitrary basis.

It is now evident that infrared-sensitive massive cathodes can be prepared by approaching the desired state from either side of the cesium-oxygen phase diagram. In Section 3.1 a number of examples were given in which infrared-sensitive cathodes were prepared by approaching



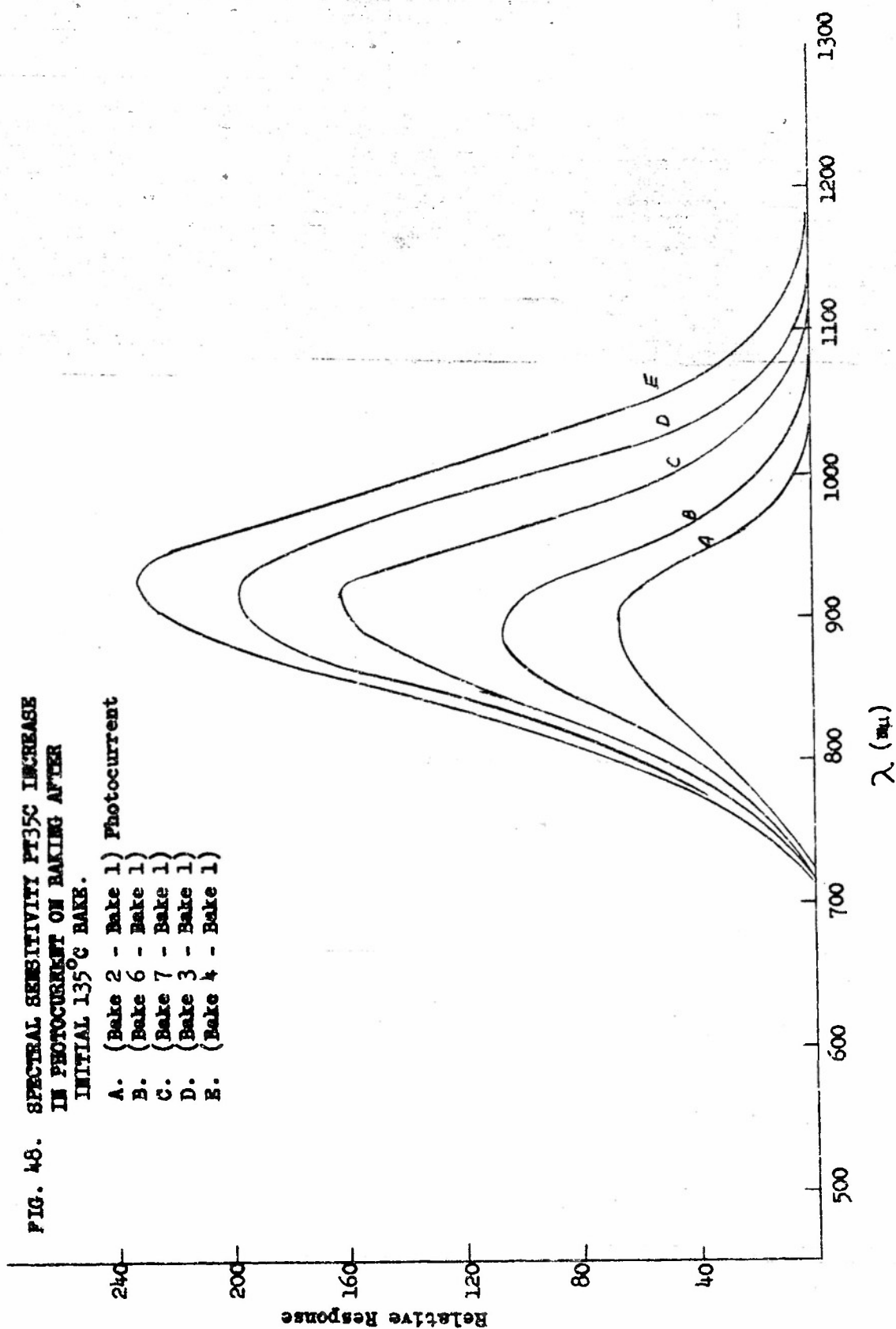


FIG. 48. SPECTRAL SENSITIVITY PT35C INCREASE  
IN PHOTOCURRENT ON BAKING AFTER  
INITIAL 135°C BAKE.

- A. (Bake 2 - Bake 1) Photocurrent
- B. (Bake 6 - Bake 1)
- C. (Bake 7 - Bake 1)
- D. (Bake 3 - Bake 1)
- E. (Bake 4 - Bake 1)

the desired state from one side and PT35C provides an example in which approach takes place from the opposite side. The results obtained for PT35C strongly suggest that  $\text{Cs}_2\text{O}$  is involved in the production of photoelectrons on illumination with infrared radiation. We note, however, the very great difference between the results obtained for PT35C and those obtained with the semitransparent cathode PT26 discussed in the previous section. This difference strongly suggests that  $\text{Cs}_2\text{O}$  alone is not enough to ensure high infrared sensitivity, a result which agrees well with previous work as outlined in Section 1.

### 3.4 Baking and Excess Cesium

In Section 3.1 we have outlined at some length a theory of cathode composition in which it is proposed that cathodes, prepared to maximum thermionic emission, contain two oxides of cesium. One of these,  $\text{Cs}_2\text{O}$  (mixed with silver) constitutes the source of photoelectrons while the other (a higher oxide of cesium) serves as a "regulator" which at equilibrium fixes the concentration of "adsorbed cesium" at (or near) its optimum value. (The term "adsorbed cesium" has been previously discussed in Section 3.1 and its significance will be further clarified in Section 3.7 after more experimental results have been presented.) If this view is correct then an important function of a baking operation is to establish equilibrium, or an approximation to equilibrium, in the cathode provided, of course, that the baking operation is not so prolonged or conducted at such a high temperature as to bring about extensive reaction with the glass envelope of the cathode. Moreover, it was pointed out in Section 3.1 that the cathode reactions are slow even at  $190^\circ\text{C}$  and are no doubt very much slower at room temperature. As a test of the above proposal we have therefore performed several experiments in which very small amounts of cesium are added to the cathode at room temperature. If (1) the cathode reactions are actually slow at room temperature and (2) the cathode contained the optimum amount of "adsorbed cesium" as the result of a preceeding equilibrating bake then the addition of cesium at room temperature should reduce the infrared sensitivity (due to exceeding the optimum "adsorbed cesium" combination) and the infrared sensitivity should be recovered on rebaking the cathode since this re-establishes equilibrium between the higher cesium oxide, "adsorbed cesium", and  $\text{Cs}_2\text{O}$ . The results of such an experiment are given in Section 3.4.1 below and the above predictions are confirmed. Moreover, the change



in spectral response brought about by a slight excess of "adsorbed cesium" is very clearly revealed.

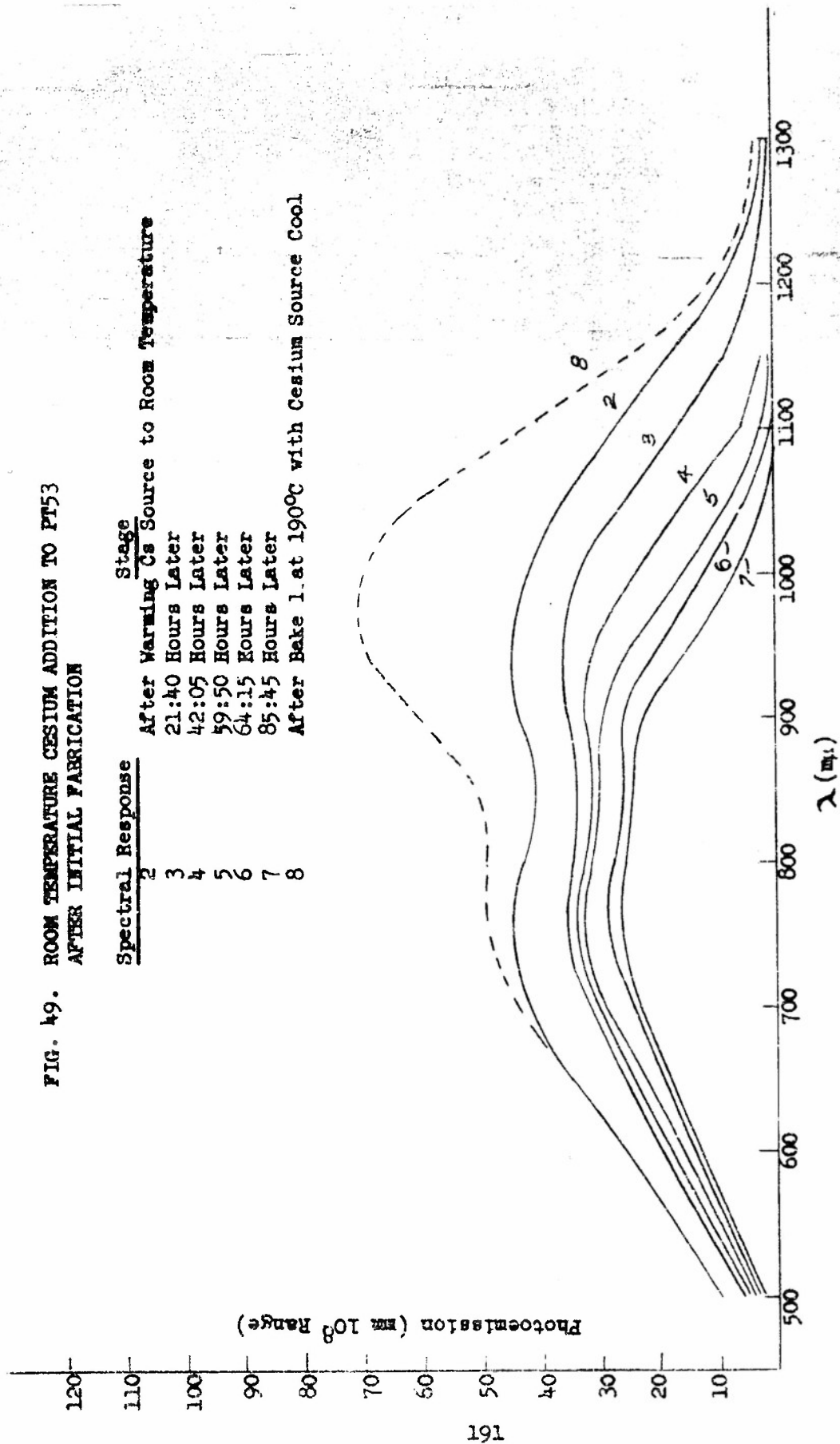
In Section 3.42 are given the results obtained on baking a series of cathodes in which equilibrium is apparently not established, probably because the rate of addition of cesium to the cathodes was much higher than in the preparation of the cathode mentioned above. The cathodes of Section 3.42 are massive cathodes but the method of preparation is similar to that of semitransparent cathodes, outlined in Section 1.2, at least in the manner in which the extent of cesium addition is controlled. The results seem to have some practical value in indicating the effect of baking on such cathodes.

#### 3.41 Room temperature Cs addition

During the fabrication of cathode PT53, two experiments were performed which illustrate the effect of room temperature cesium addition on the photoemission. In the fabrication of PT53 at 150°C the cathode was oxidized to a second order yellow color corresponding to  $9.84 \times 10^{-6}$  gramatoms of oxygen. Cesium was added to the tube at a rate of  $6.13 \times 10^{-8}$  mole per minute at 150°C (7 cathode monolayers per minute) and at a rate of  $1.6 \times 10^{-11}$  moles per minute at room temperature. Tube PT53 was of the type used in Section 3.1 for the study of the development of thermionic and photoelectric emission.

In the initial fabrication of PT53 the cesium addition was discontinued shortly beyond the thermionic emission maximum and the tube stabilized at 150°C. After cooling the tube to room temperature the spectral response was measured and the cesium source was cooled over night with a dry ice-acetone mixture. No change in spectral response took place on standing. This shows that the tube is stable as long as cesium is not being added. The following day the cesium source was warmed to room temperature and the change in spectral response with time determined. The change in the spectral response during 85.75 hours of cesium addition is shown by curves 2 through 7 in Fig. 49. After the response had changed to curve 7 the tube was rebaked at 190°C with the cesium source cool to give the final response curve 8. The thermionic and photoelectric emission during the 190°C

FIG. 49. ROOM TEMPERATURE CESIUM ADDITION TO PT53  
AFTER INITIAL FABRICATION



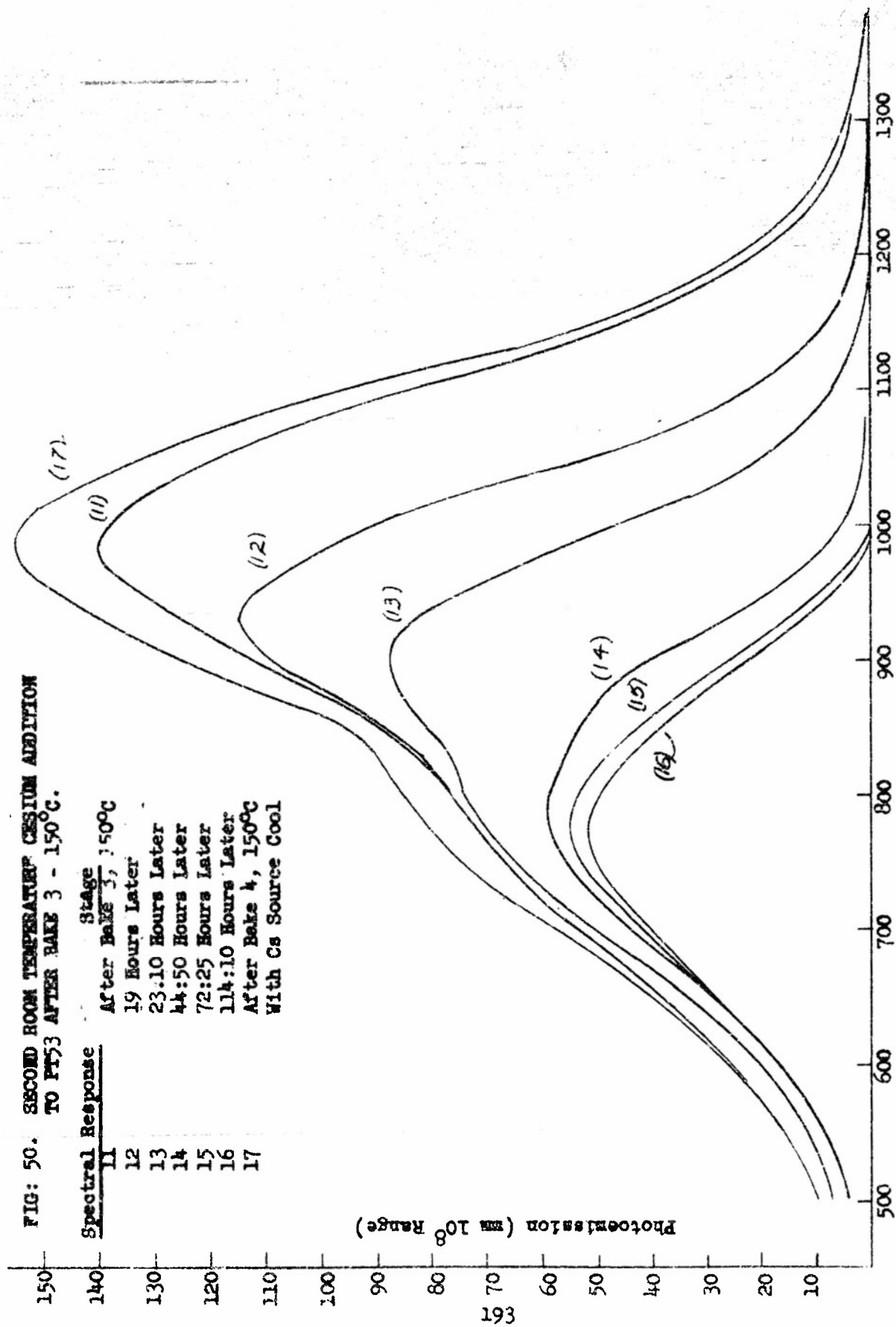
bake increased to stable maximum values. During the room temperature cesium addition the tube gross composition was changed from 1.609 to 1.617 (Cs/O).

During bake 3 (at 150°C) cesium was added to the tube (PT53) to give a gross composition of 2.062. After cooling the cesium source the photosurface was stabilized at 150°C and the tube finally cooled to room temperature. During cesium addition to this surface at room temperature the spectral response of the tube changed from curve 11 to 16 in Fig. 50. The tube was then rebaked at 150°C to constant thermionic and photoelectric emission with the cesium source cool. As shown in Fig. 50 the baking resulted in the recovery of the original spectral response. The room temperature cesium addition corresponded to a change of the (Cs/O) mole ratio from 2.062 to 2.072.

Before discussing the above results several features of the response curves immediately after baking deserve comment. Curve 2 of Fig. 49 contains two maxima one at 750  $m\mu$  and the other at 950  $m\mu$ . This again emphasizes the possibility of two types of emitting centers which has already been pointed out in Section 3.2 in the discussion of tube PT24C and further suggested by the spectral responses of Fig. 46 for PT35C. We note in passing that double maxima similar to curve 2 of Fig. 49 have also been obtained for other tubes with a relatively low (Cs/O) ratio ( $\sim 1.0$ ) and when such tubes are cooled to room temperature there is generally an appreciable increase in ( $F_1$ - $F_2$ ) response. The reason for such behavior is not entirely clear.

The spectral response for the cathode after the third bake (curve 11 Fig. 50) no longer has a double maximum although an inflection is evident in the vicinity of 750  $m\mu$  thus suggesting that two types of emitting centers are still present although the effect of one type is somewhat obscured by the predominance of the other. Curve 11 of Fig. 50 is typical of a good infrared-sensitive massive cathode with a maximum at 985  $m\mu$ , half maximum at 1115  $m\mu$ , and long wavelength limit of 1450  $m\mu$ .

It has previously been pointed out in Section 3.12 that tube PT53 repeatedly recovered high infrared sensitivity on cooling the cesium source and cooling the tube throughout the composition range  $1.6 < (\text{Cs/O}) < 2.8$ .



This is not due to the fact that  $\text{Cs}_2\text{O}$  is infrared-sensitive (see Section 4.23) but is probably due to the fact that cesium collects on the tube envelope as well as the cathode so that the gross (Cs/O) ratio is considerably greater than the cathode (Cs/O) ratio. It must be emphasized that tube PT53 gave no indication of being an abnormal tube. In particular no indication of a leak was obtained at any stage. So much data were accumulated on this tube that a number of important points were established and hence the repeated references to the results throughout this report.

The data of Figs. 49 and 50 clearly show how markedly a small amount of cesium can affect infrared sensitivity. It is also evident that infrared sensitivity is readily restored by heating the tube to a low temperature for a short time. As the results of Section 3.1 show, the cathode reactions are slow even at high temperatures and the rate of reaction of cesium must be very slow indeed at room temperature. The changes of Figs. 49 and 50 are almost certainly due therefore to the accumulation of a layer of "adsorbed" cesium on the cathode surface. The recovery on baking is easy to understand. For the cathode still contains an oxidizing agent (a higher oxide of cesium) which reacts with adsorbed cesium at an appreciable rate on baking. Thus reducing the concentration of adsorbed cesium to its optimum value. The fact that the gross (Cs/O) ratio slightly exceeds 2 in one case does not render this argument invalid since a considerable proportion of the total cesium is on the tube envelope rather than the cathode. It is quite interesting that cesium addition tends to affect the maximum at 950  $\text{m}\mu$  more strongly than that at 750  $\text{m}\mu$ . In both Figs. 49 and 50 the response seems to approach to one with a maximum at 750  $\text{m}\mu$  and a long wavelength limit of 900 - 1000  $\text{m}\mu$ . This is remarkably similar to the Class II response for PT24C (Section 3.2) and, moreover, the similarity to the long wavelength maxima listed in Table IV is quite clear. It is notable that several of the investigators listed in Table IV reported that their photocathodes contained excess cesium, e.g. 7% excess was reported by Prescott and Kelly. This response with a 750  $\text{m}\mu$  maximum is frequently encountered and seems to some degree unique. It must be added, however, that the addition of large excesses of cesium, in other experiments, shifts the response maximum to about 650  $\text{m}\mu$  and the long wavelength limit to 800  $\text{m}\mu$ . Inspection of Figs. 49 and 50 shows at once why the accumulation of a thin layer of cesium on

the cathode during processing so reduces the infrared sensitivity, as discussed in Section 3.1. The spectral response curves 4 and 7 of Fig. 46, for PT350, also become understandable at once in terms of these results. The theory mentioned in the introduction to the present section seems to be confirmed.

The change in photoemission at 900 and 1000  $m\mu$  during the room temperature cesium addition to PT53 is shown in Fig. 51 as a function of the amount of cesium added. The infrared sensitivity is practically eliminated before the equivalent of a cesium monolayer had been deposited over the interior surface of the tube (envelope and cathode). It is thus apparent that a cathode stable at room temperature may not be obtained if any cesium source exists in the tube.

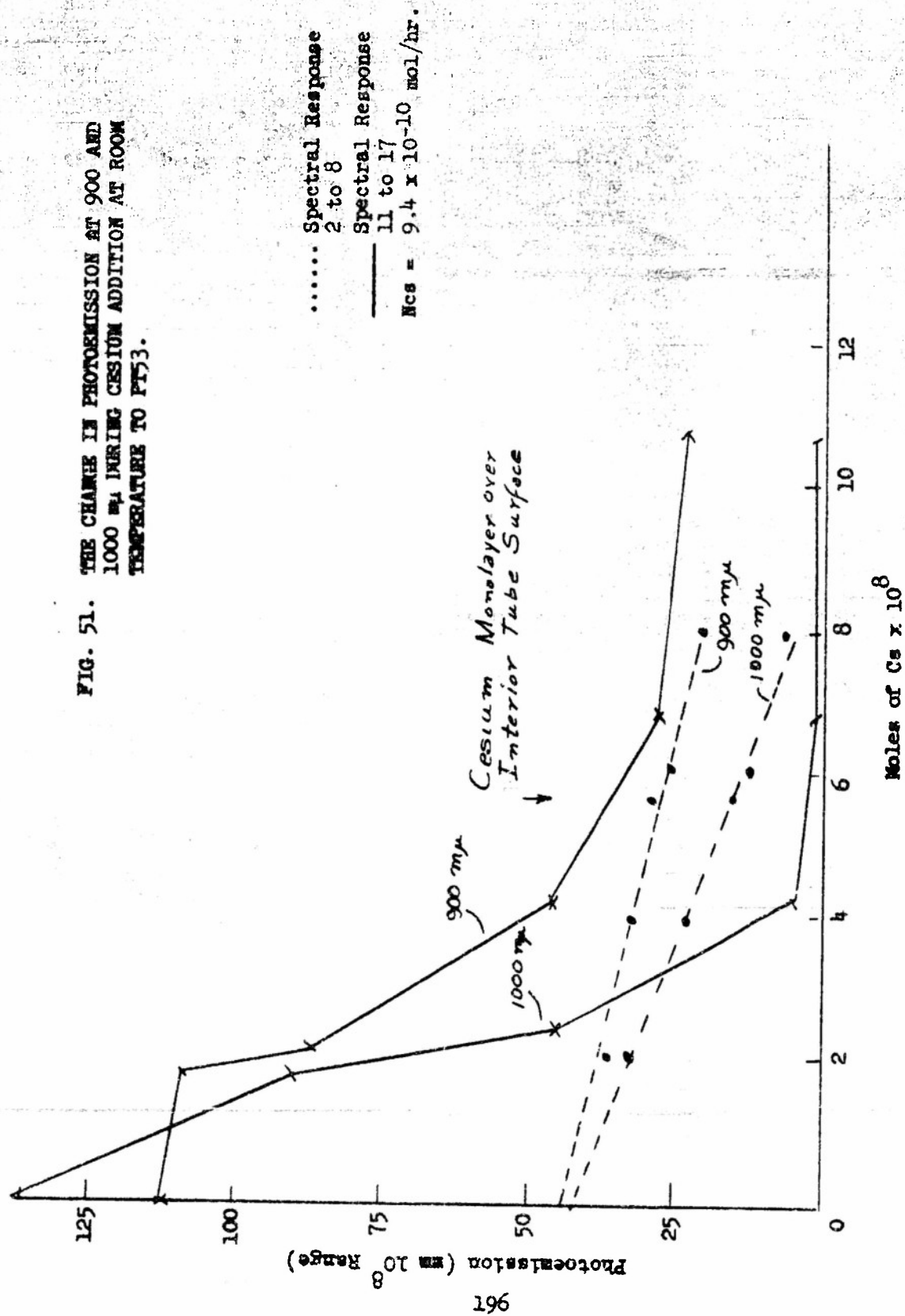
The loss in sensitivity during the cesium addition to the high infrared-sensitive surface is even more clearly shown by the difference curves in Fig. 54. The progressive loss of infrared response corresponds rather closely to the gain obtained during the high temperature distillation of excess cesium away from the photosurface discussed in Section 3.22. However, the two cases are not chemically equivalent. The recovery on baking the surface with a small amount of surface excess cesium is rapid even at only 130°C. Where a large excess is present, as in Section 3.22, the photoemission may not be readily recovered by even prolonged baking at low temperatures ( $\sim 130^\circ\text{C}$ ). This difference is due to the fact that the surface to which a small amount of cesium was added contained an oxidizing agent, namely cesium oxides higher than  $\text{Cs}_2\text{O}$ . When large excesses are present, removal of the excess requires distillation away from the surface to a trap or to the tube wall.

#### 3.42 Baking and infrared sensitivity

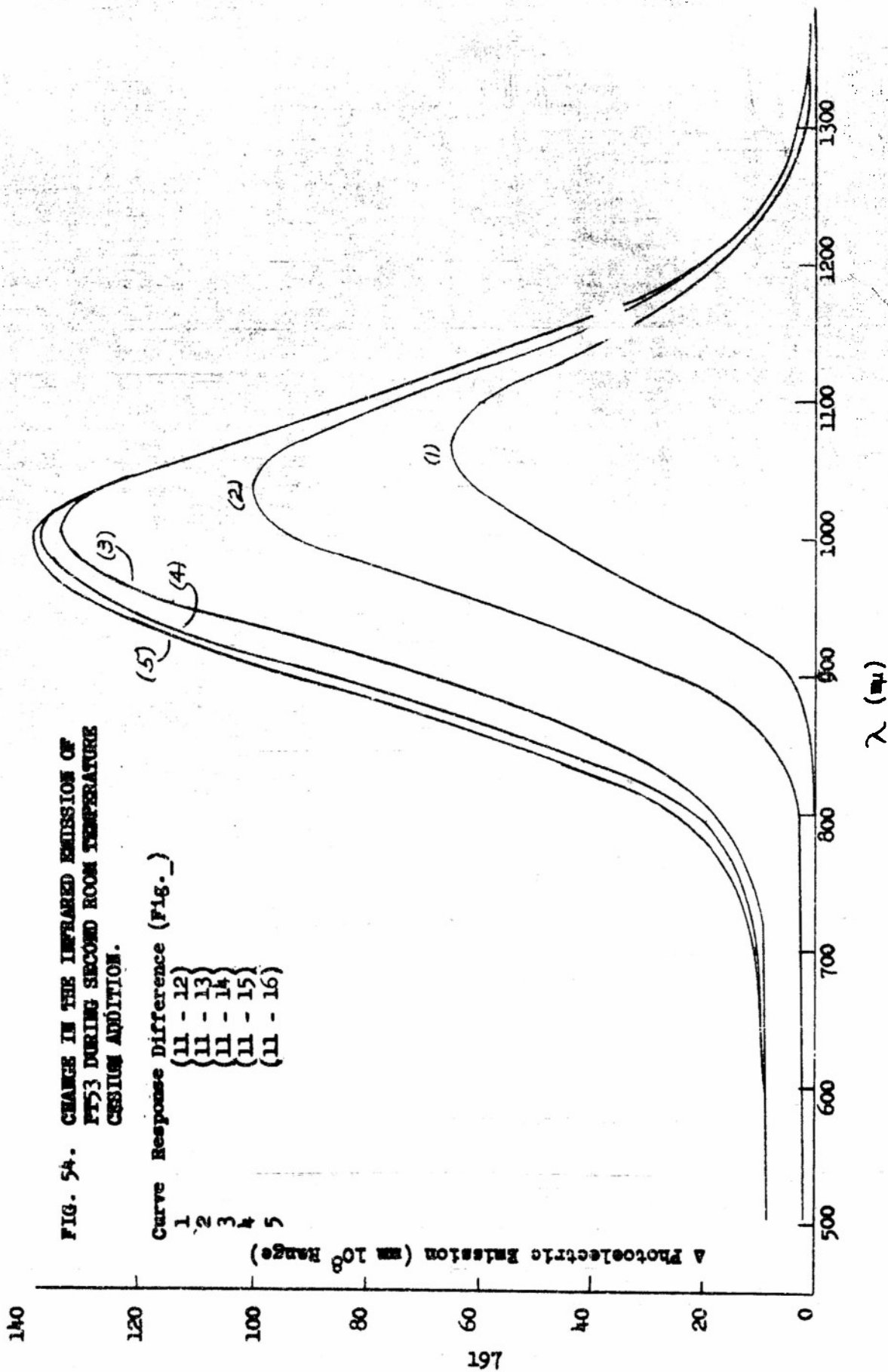
The cathodes which have been described thus far have been prepared under rather carefully controlled conditions. The tubes for the most part were processed without completely sealing off the cesium source. It is therefore of interest to now briefly consider cathodes prepared under conditions even more closely comparable to commercial processing conditions. In this case cesium may be added while the phototube is still attached to the vacuum system, until the maximum thermionic emission is reached. At this point the cesium source is cooled and



FIG. 51. THE CHANGE IN PHOTOEMISSION AT 900 AND 1000 mμ INCREASING CESIUM ADDITION AT ROOM TEMPERATURE TO PT53.







after the thermionic emission passes a second maximum the tube is cooled. (This method of control is especially prevalent in the preparation of semitransparent cathodes.) After sealing off the cesium source the tube is sealed off the vacuum system. At this stage the cathode frequently exhibits a low sensitivity and a spectral response which changes with time at room temperature. Consequently the cathode is given a "stabilizing" bake in order to obtain constant response. Since the tube remains attached to the vacuum line throughout the cesium addition it is clear that composition is not determined. The only control is exercised by measurement of thermionic emission. These tubes are obviously much less well characterized than those of previous sections.

The variety of spectral response characteristics which may be obtained during the fabrication of such tubes is illustrated by the data obtained during the preparation of tubes PT36, PT37, PT1588-93 and PT1588-98. The first two tubes are massive silver cathode tubes formed on a base of sheet silver; whereas the latter two are tubes formed on bases of thick evaporated silver film using the tube design of Fig. 14. The fabrication data are summarized in Table XII. The results obtained are discussed below.

PT36C. In the fabrication of PT36C, cesium addition was continued beyond the first maximum in thermionic emission as shown in Fig. 55. The tube was cooled after the second maximum was passed, the cesium source sealed off, and the tube sealed off the vacuum system. The spectral response of PT36C after seal-off (curve 1 Fig. 56) indicates the presence of excess cesium on the surface.

The tube was first baked for 60 minutes at  $130^{\circ}\text{C}$ , and then rebaked for 100 minutes at  $130^{\circ}\text{C}$ . The spectral response after each bake is shown in Fig. 56. The long wavelength limits after the bakes were at 1300 and 1350  $\text{m}\mu$  respectively, the maximum photocurrent at 905  $\text{m}\mu$  and 915  $\text{m}\mu$  and the half maximum currents at 1005 and 1030  $\text{m}\mu$  respectively. The change in sensitivity from immediately after seal-off to the first bake is shown by the dotted curve in Fig. 56. This bake added a component of photoemission similar to the series obtained in PT35C. The suggestion of two types of emitting centers is again obvious.

After baking the cathode for 2400 minutes at  $130^{\circ}\text{C}$ , the photosensitivity decreased to curve 4 in Fig. 56. The

TABLE XII. DATA FOR COMPLETELY  
FABRICATED CATHODES.  
CESIUM SOURCE REMOVED.

Tube	Operation	Moles O <sub>2</sub> / Sq. cm x 10 <sup>7</sup>	Oxide Color	Furnace Cs Source °C	Temp. Tube °C	Time min	Wavelengths (mμ)		
							Long Limit	Max. Sens.	Max. Sens.
<u>PT36C</u>	Fab.	2.52	1st blue	132	190	-	1100	740	875
	Bake 1				130	60	1300	905	1005
	Bake 2				130	100	1350	905	1030
	Bake 3				130	2400	1150	675	805
<u>PT37C</u>	Fab.	3.93	2 <sup>nd</sup> yellow	-	185	-	1150	650	805
	Bake 1				130	30	1450	955	1078
	Bake 2				156	20	1500	960	1080
<u>PT1588-93</u>	Fab.	1.21	1st blue	130	186	-	1000	680	810
	Bake 1				125	60	1200	720	975
	Bake 2				130	60	1200	725	-
<u>PT1588-98</u>	Fab.	4.8	2 <sup>nd</sup> blue	166	180	-	1300	910	1020
	Bake 1				130	-	1350	920	1020
	Bake 2				130	-	1400	930	1078
	Bake 3				160	-	1400	940	1080
	Bake 4				180	-	1400	950	1080
	Bake 5				180	-	1450	955	1080
	Bake 6				190	-	1100	635	790

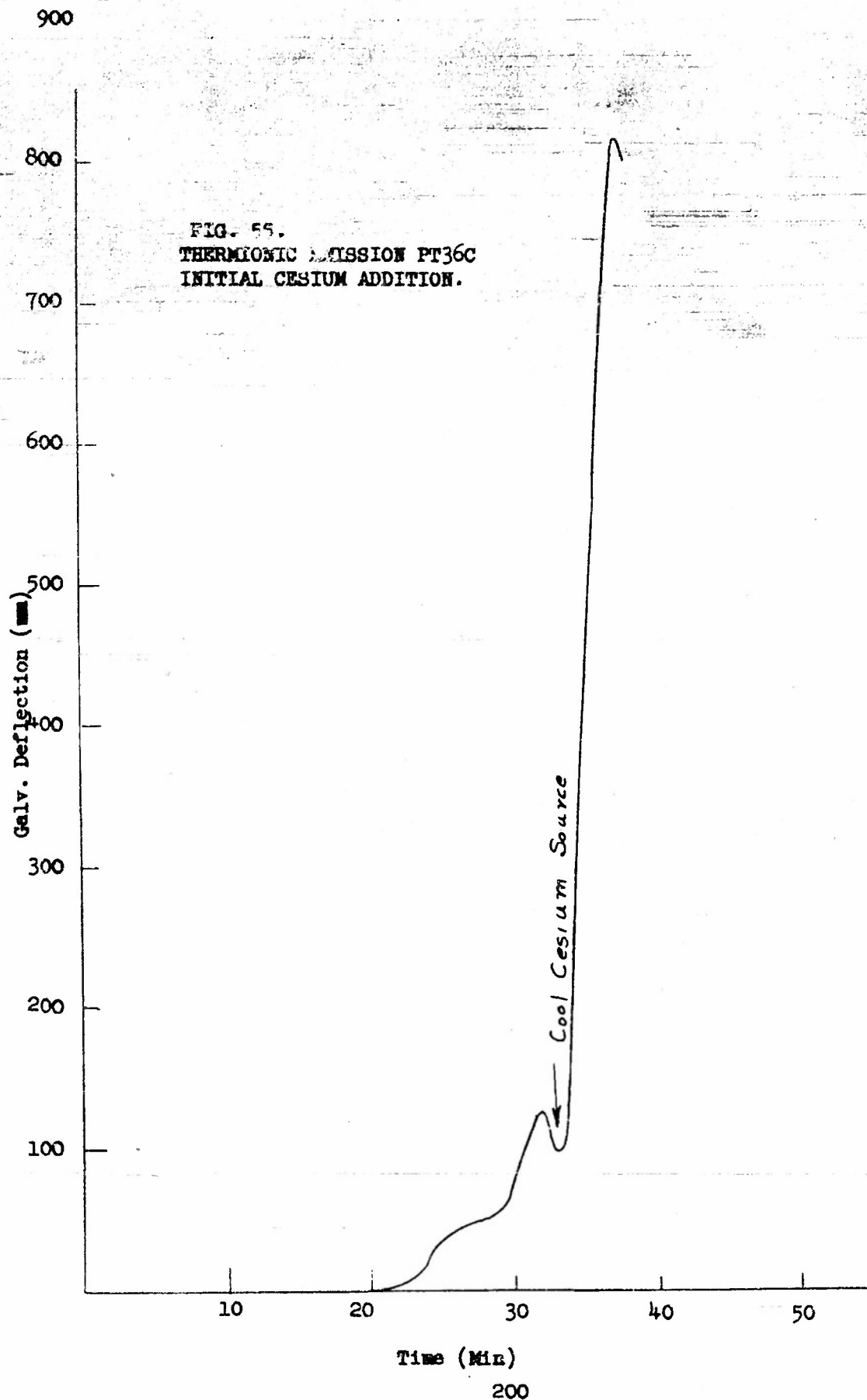
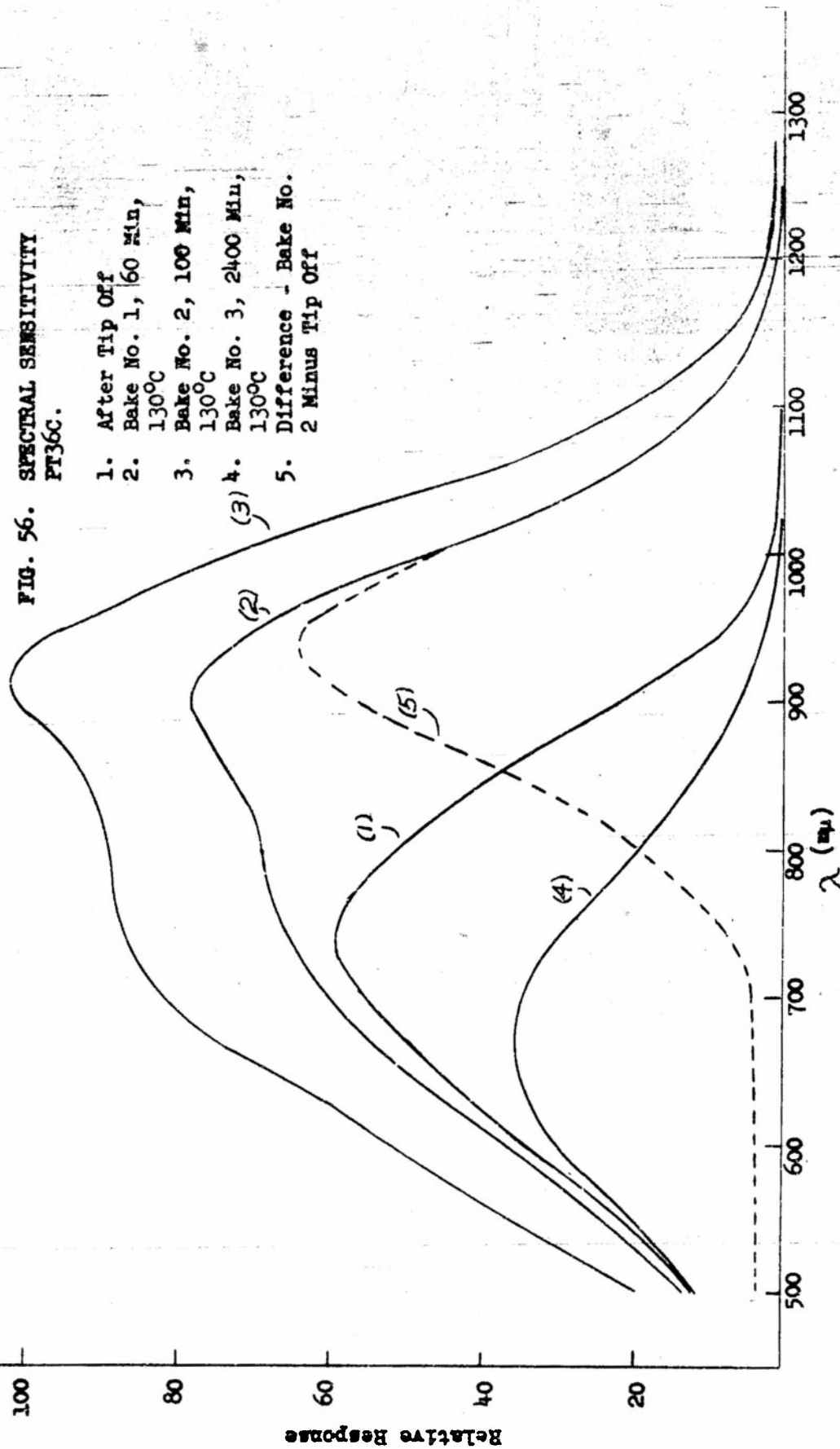


FIG. 56. SPECTRAL SENSITIVITY  
PT36C.

1. After Tip Off
2. Bake No. 1, 60 Min,  
130°C
3. Bake No. 2, 100 Min,  
130°C
4. Bake No. 3, 2400 Min,  
130°C
5. Difference - Bake No.  
2 Minus Tip Off



maximum shifted from 905 to 675  $m\mu$  and the long wavelength limit from 1350  $m\mu$  to 1150  $m\mu$ . This spectral response corresponds to the one obtained in PT24C after long baking at 180 - 190°C.

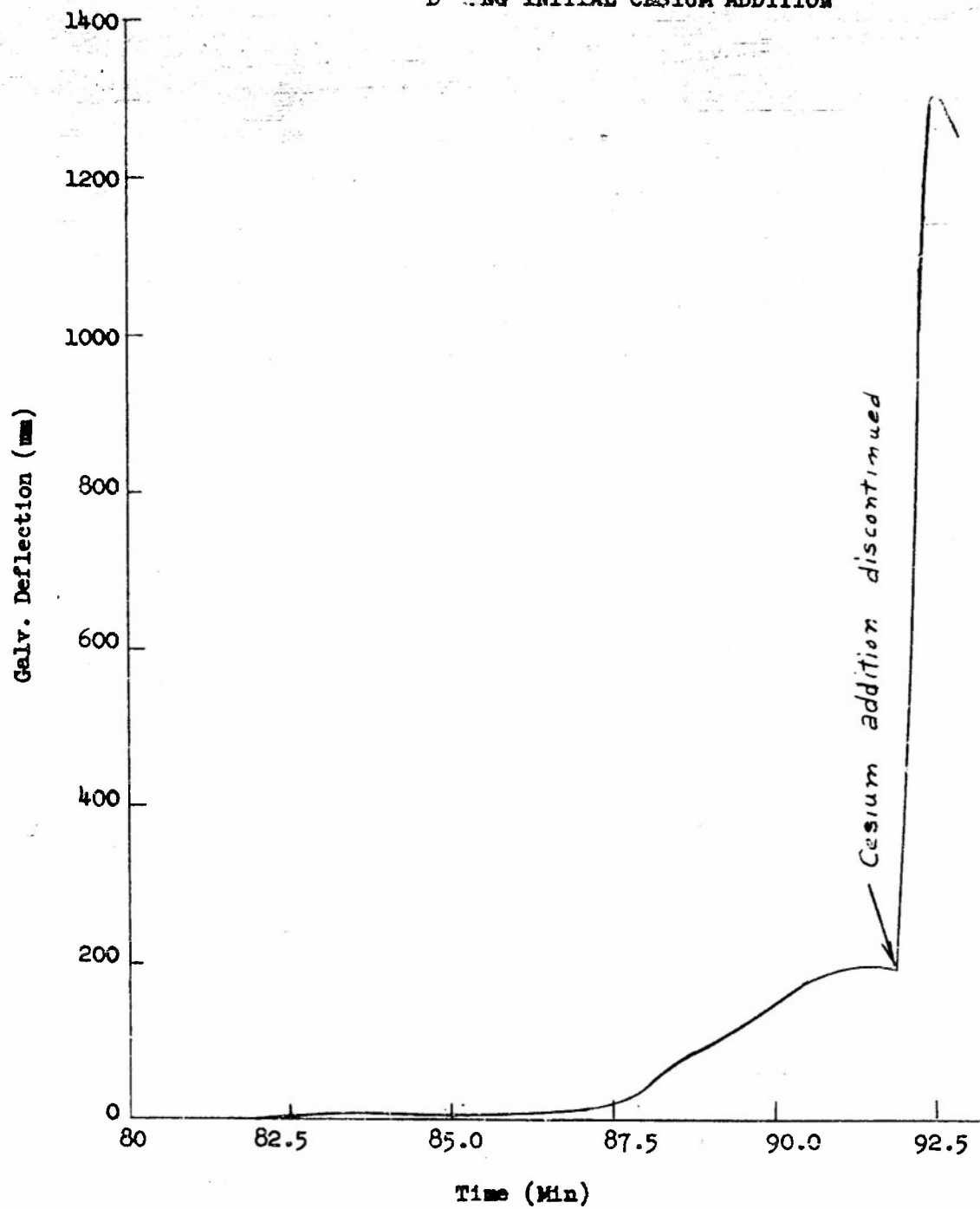
PT37C. For the cesium addition to PT37C, a cesium chromate-silicon channel (RCA part No. FZ 607E) was mounted in a side tube with a large bore connecting tube to the phototube. The rate of addition of cesium was controlled by the heating current to the channel. The addition of cesium was discontinued at the first maximum in thermionic emission. When the cesium addition was stopped the thermionic emission rapidly increased to a second maximum as shown in Fig. 57. The tube was cooled immediately after passing this second maximum. The spectral response, after tip off, had a maximum at 650  $m\mu$  and a long wavelength limit of 1150  $m\mu$  (Fig. 58).

After the tube was baked to constant thermionic emission at 130°C, a good infrared-sensitive surface was obtained as shown in Fig. 58. For this surface, the photoemission maximum was at 955  $m\mu$ , the half maximum wavelength at 1078  $m\mu$ , and the long wavelength limit was 1450  $m\mu$ .

The tube was then rebaked to constant thermionic emission at 156°C. In order to obtain data for the computation of the thermionic work function, the thermionic emission at a series of lower temperatures was measured. This second bake resulted in very small changes in spectral response as shown by the difference curve for bakes 1 and 2 at the top of Fig. 58.

The thermionic current is plotted on a log scale as a function of the reciprocal of the absolute temperature in Fig. 59. The corresponding thermionic work function was 0.51 ev. In the figure it is of interest to note that the point for the final thermionic emission at 185°C before cooling the tube lies on the curve defined by the lower temperature bake data. This fact suggests that the surface obtained on removal of the superficial cesium layer by baking corresponds to the high temperature thermionic emitting surface. Thus, considering the reversible loss of infrared sensitivity with increased temperature, the interesting situation exists where the infrared sensitivity decreases with increasing temperature while the thermionic emission increases markedly.

FIG. 57. THERMIONIC EMISSION PT37C  
DURING INITIAL CESIUM ADDITION





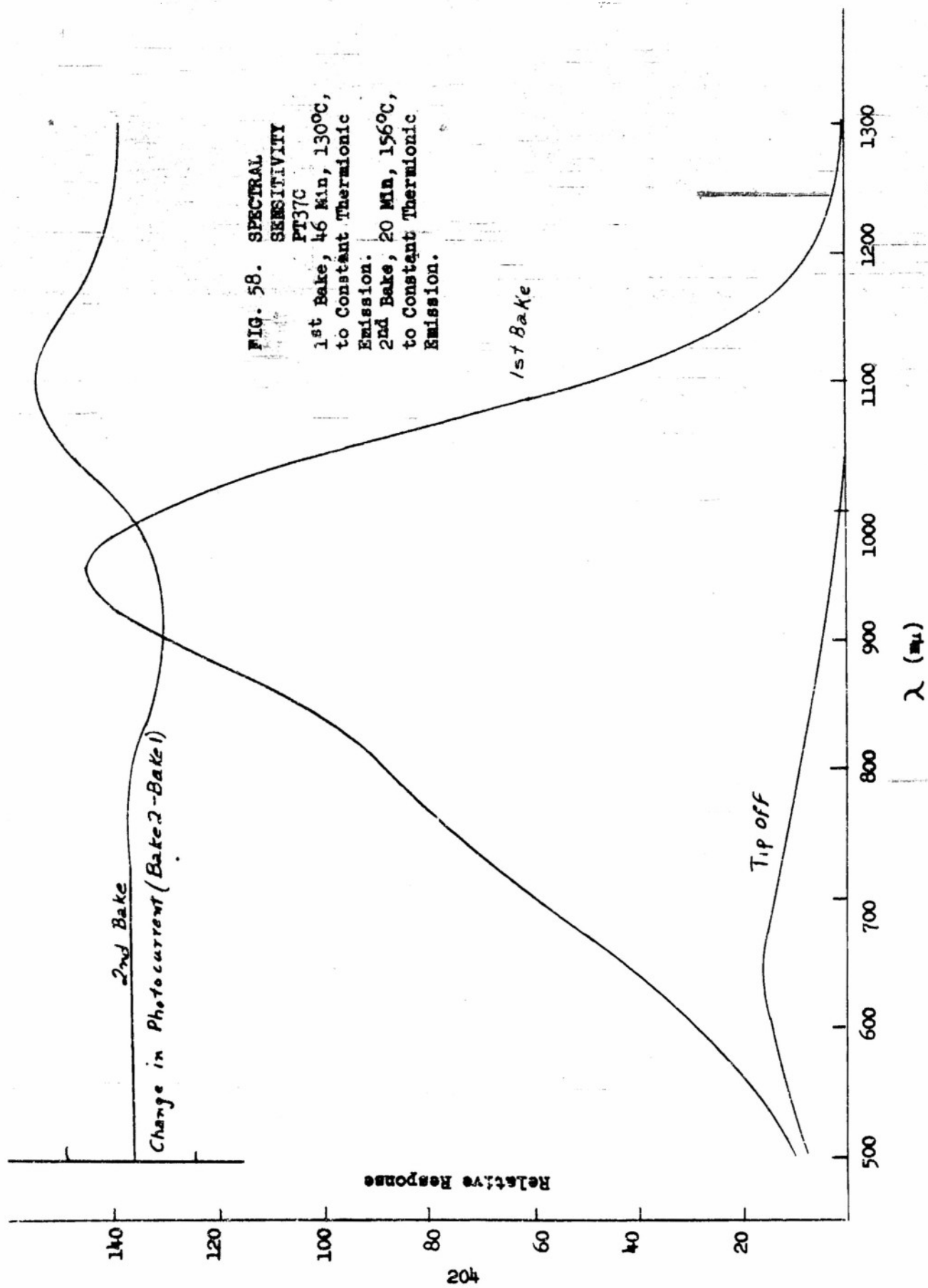
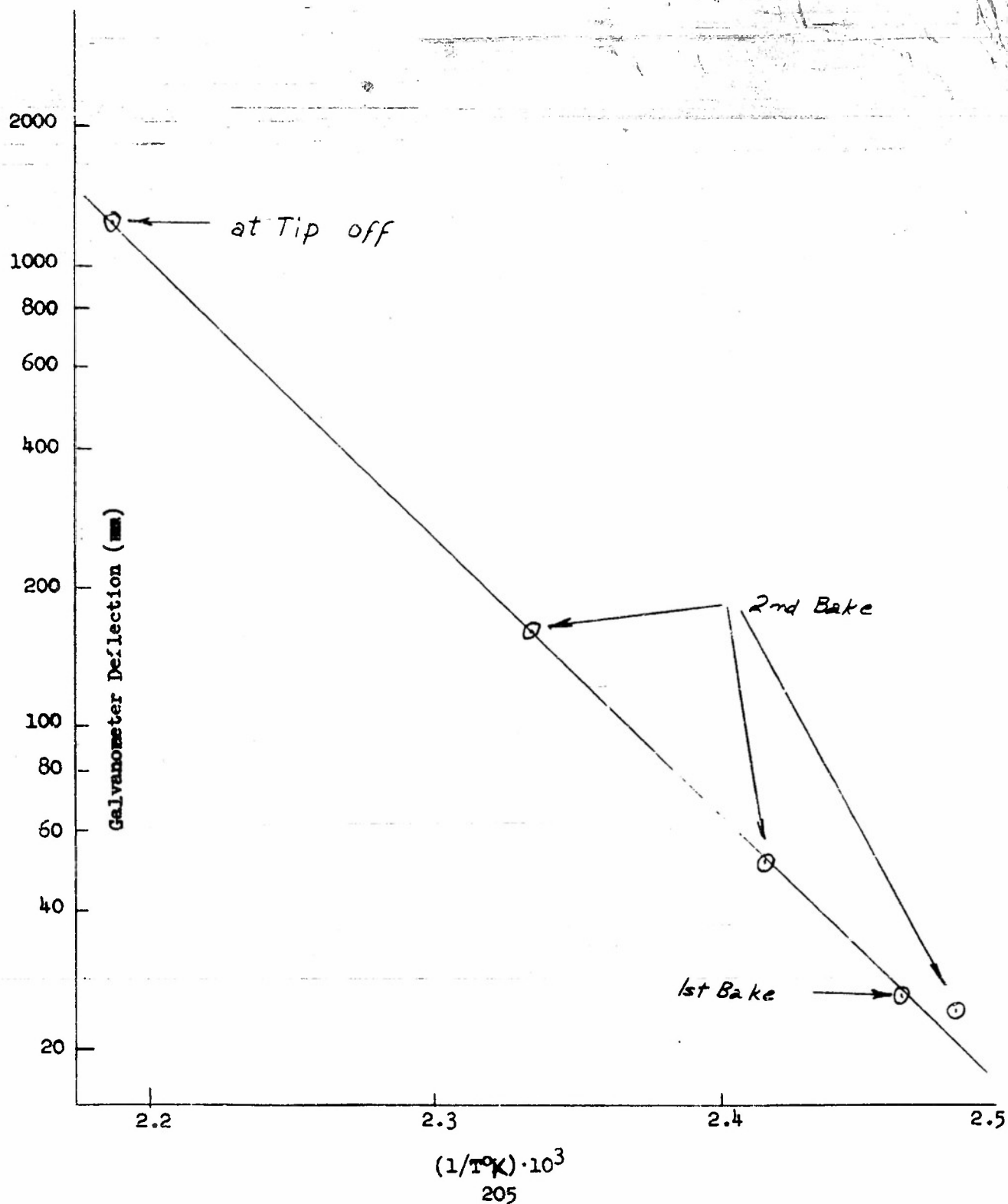


FIG. 59. THERMIONIC EMISSION VERSUS THE  
RECIPROCAL OF THE ABSOLUTE  
TEMPERATURE - PT37C.

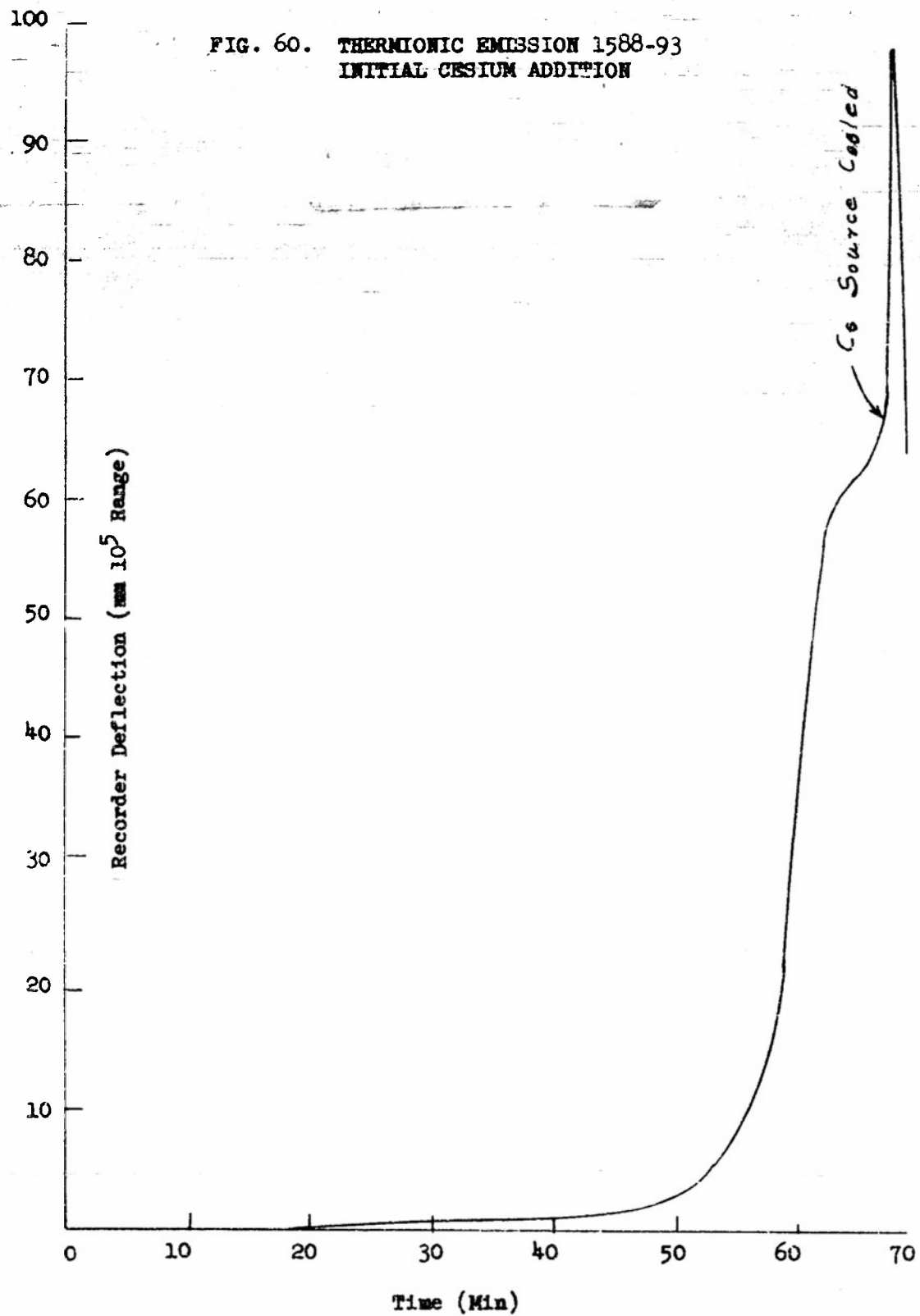


PT1588-93. In the massive cathode tubes PT1588-93 and PT1588-98, the cathode was a thick silver film deposited on a microscope cover glass, which was then mounted on a tantalum clip support (see Fig. 14). During the fabrication of PT1588-93 the cesium addition was discontinued before the first maximum thermionic emission. After discontinuing the cesium addition, the thermionic emission increased to a maximum and then rapidly decreased as shown in Fig. 60. The spectral response after tip off (Fig. 61) is similar to that observed in PT36 and PT37. This distribution is interpreted as resulting from a thin layer of excess cesium on the cathode. The layer probably results partly from distillation of cesium onto the cathode during sealing off from the vacuum system and sealing off the cesium source.

Baking the cathode for 1 hour at 125°C resulted in an increase in the photoemission. The spectral response measurement showed that the cathode was least sensitive at the bottom and the greatest at the top as shown by curves 1A, 2A, 3A in Fig. 61. After a second bake of 1 hour at 130°C there was a marked decrease in the infrared sensitivity as shown by curves 1B, 2B, and 3B in Fig. 61. Thus a process was occurring during the baking operation which tended to destroy the infrared sensitivity during baking at 130°C. The conditions leading to this loss are not understood at the present. It has been observed that the time required to destroy the infrared sensitivity of cathodes prepared under carefully controlled processing conditions is quite long at 130°C. Considering the experimental conditions it appears probable that the decline on baking is the result of chemical reactions at the photosurface rather than a mere change in cathode micro structure. The variation in sensitivity with cathode area was related to the oxidation of the silver surface. During the assembly of the tube, the cathode became heated so that the silver at the top recrystallized to a coarse grain structure while the bottom surface remained a smooth reflecting film. The appearance after oxidation suggested that the depth of oxidation was greatest at the top of the cathode.

PT1588-98. In the glow discharge oxidation of the PT1588-98 cathode,  $4.8 \times 10^{-7}$  moles/cm<sup>2</sup> of oxygen (O<sub>2</sub>) were deposited. In the activation step, the cesium addition was continued slightly beyond the first maximum in thermionic emission as shown in Fig. 62. The spectral sensitivity of the cathode

FIG. 60. THERMIONIC EMISSION 1588-93  
INITIAL CESIUM ADDITION



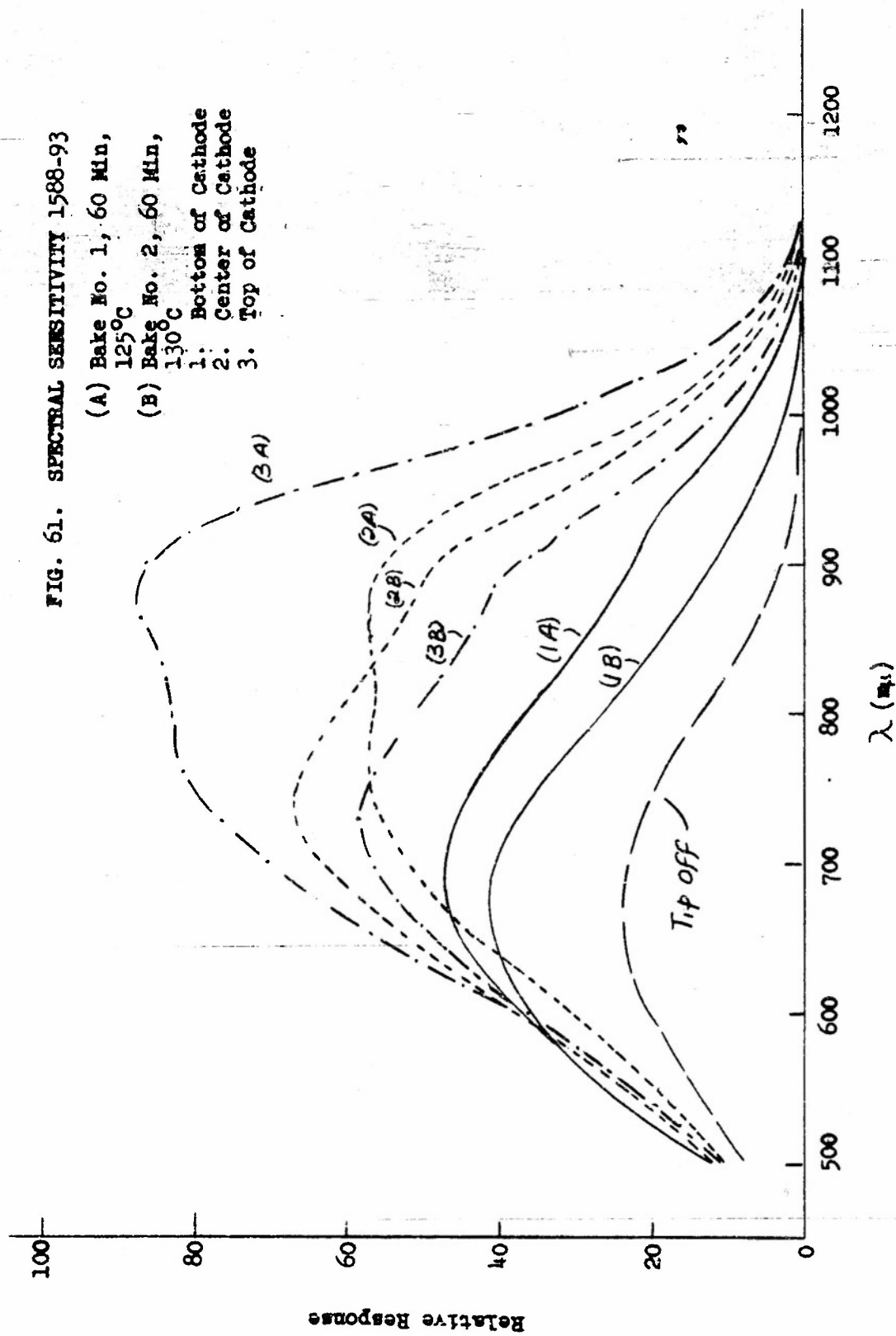
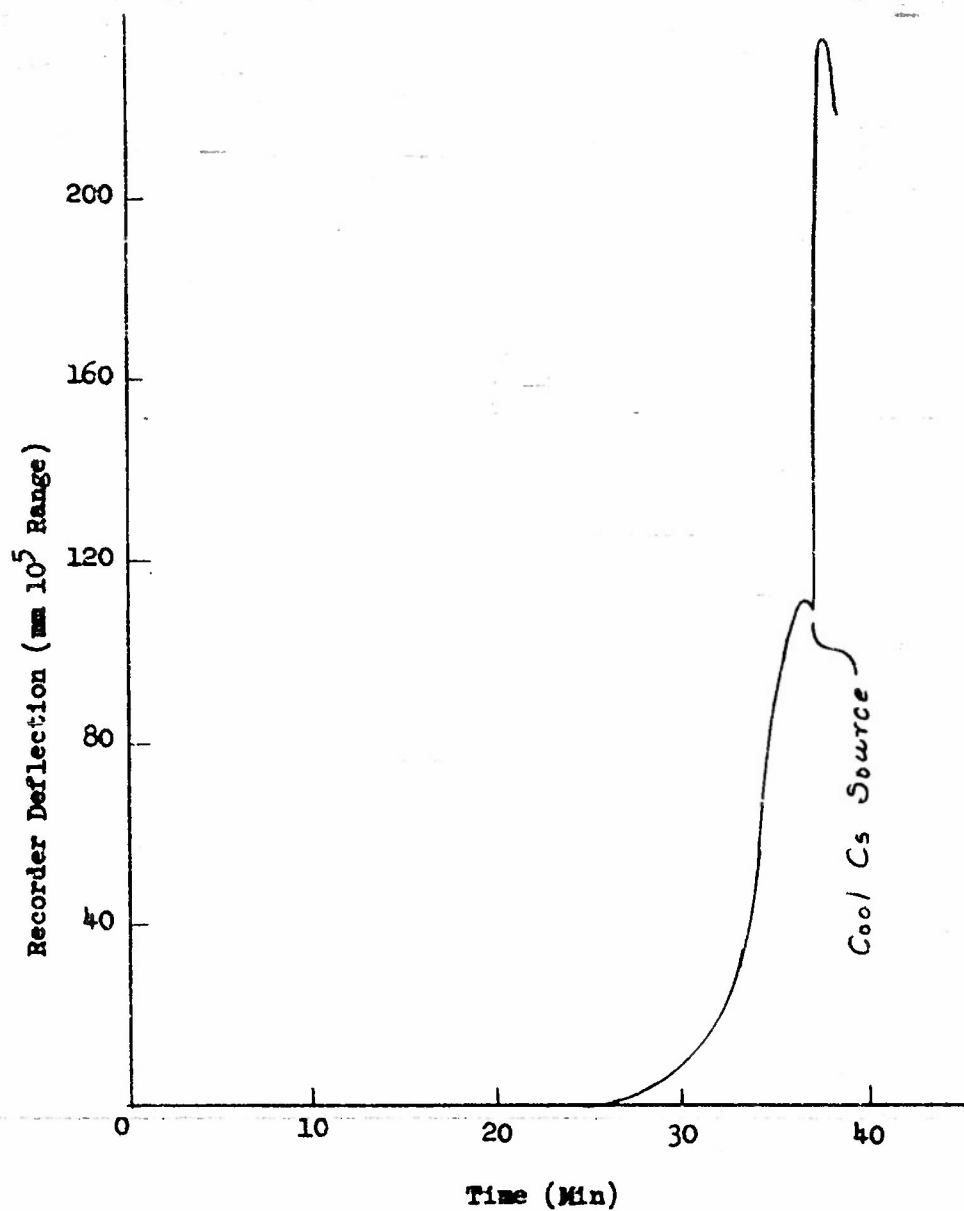


FIG. 62. THERMIONIC EMISSION 1583-98  
INITIAL CESIUM ADDITION



after sealing off from the vacuum system had a rather flat peak extending from 725 to 920  $m\mu$  as shown by curve 1 Fig. 64. Immediately after seal-off, the sensitivity maximum was at 910  $m\mu$ , the long wavelength limit at 1300  $m\mu$ , and the half maximum photocurrent wavelength at 1020  $m\mu$ .

The thermionic emission versus time curves for the first bake of 98 minutes at 130°C, and the second bake of 100 minutes at 130°C are shown in Fig. 63. During the second bake at 130°C, the thermionic emission became constant and the tube was baked at a series of lower temperatures in order to obtain data for computing the thermionic work function. The change in sensitivity of the cathode during these bakes was rather small as shown by curves 2 and 3 Fig. 64. After the second bake the photocurrent maximum was at 930  $m\mu$ , the long wavelength limit at 1400  $m\mu$  and the half maximum current wavelength at 1078  $m\mu$ . The thermionic work function after the second 130°C bake was 0.84 ev. (1480  $m\mu$ ) determined from a graph of  $\log I$  versus the reciprocal of the absolute temperature. The result may be compared to the observed long wavelength limit of 1400  $m\mu$  (0.88 ev.). The true photoelectric threshold is at shorter wavelengths, but the actual difference in the two work functions is small compared to that for PT37C. In PT37C, the thermionic work function was 0.51 ev. (2420  $m\mu$ ), whereas the observed long wavelength limit was 1500  $m\mu$  (0.83 ev.). Thus, corresponding to only a small difference in the observed long wavelength limits, there is a large difference in the thermionic work functions.

By baking the tube at a series of higher temperatures, the infrared sensitivity was further increased as shown by curves 4, 5, and 6 in Fig. 64. The corresponding thermionic emission curves for bakes 3 at 160°C and 4 and 5 at 180°C are shown in Fig. 63. It is of interest to note that the thermionic emission in bake 5 (180°C) had decreased to half the maximum value and was 2/5 of the final thermionic emission after bake 4 (180°C) but the photoemission after bake 5 was greater than for bake 4. This result also suggests that a 1:1 correspondence between photoemission and thermionic emission does not exist for this photosurface.

The tube was then baked at 190°C until the rate of decrease of the thermionic current with time became small (curve 6 Fig. 63). This bake markedly decreased the photosensitivity of the tube as shown by curve 7 Fig. 64.



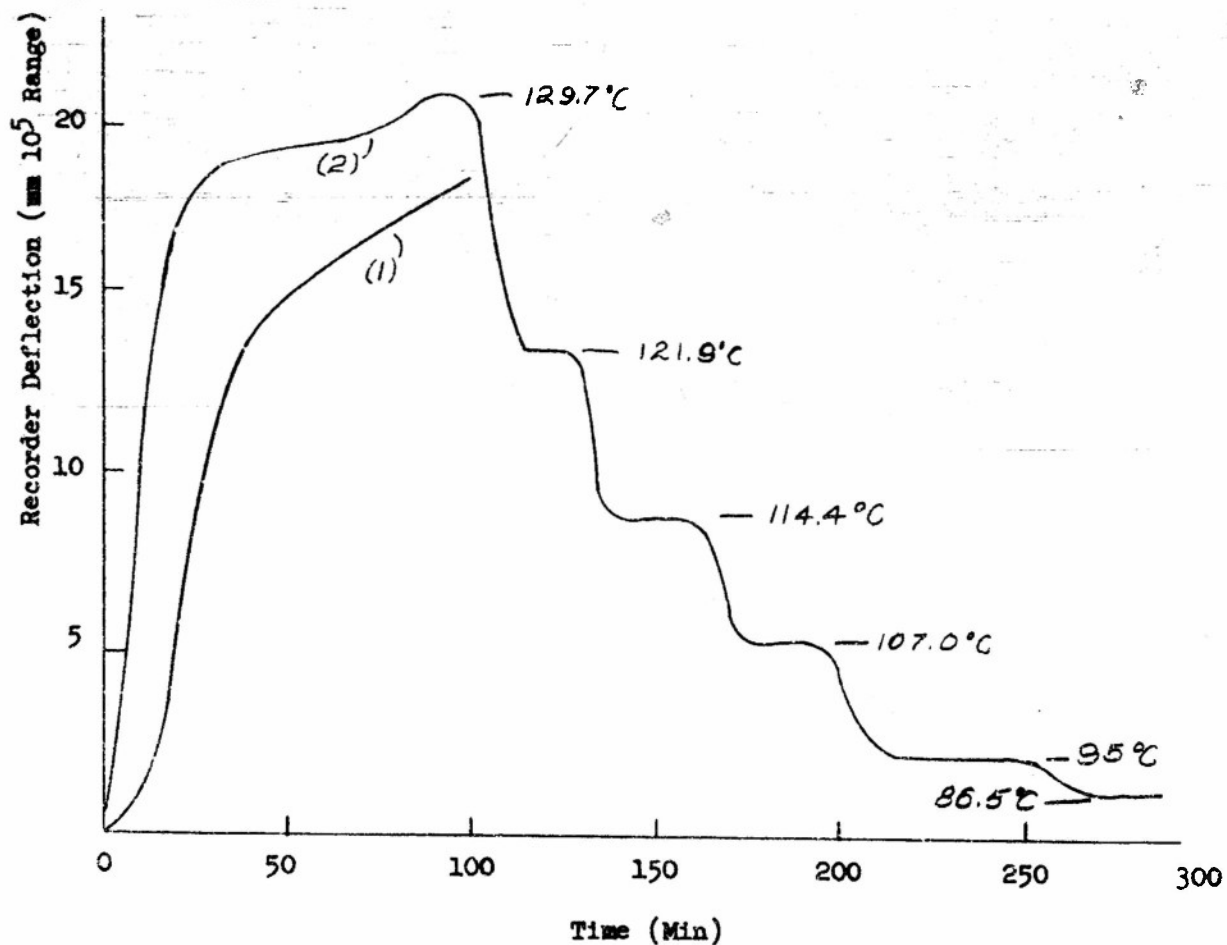


FIG. 63a. THERMIONIC EMISSION 1588-98

1 - Bake No. 1 - 98 Min, 130°C  
 2 - Bake No. 2 - 130°C

FIG. 63b. THERMIONIC EMISSION 1588-98

- 3 - Bake No. 3 - 63 Min, 160°C  
4 - Bake No. 4 - 26 Min, 180°C  
5 - Bake No. 5 - 75 Min, 180°C  
6 - Bake No. 6 - 153 Min, 190°C

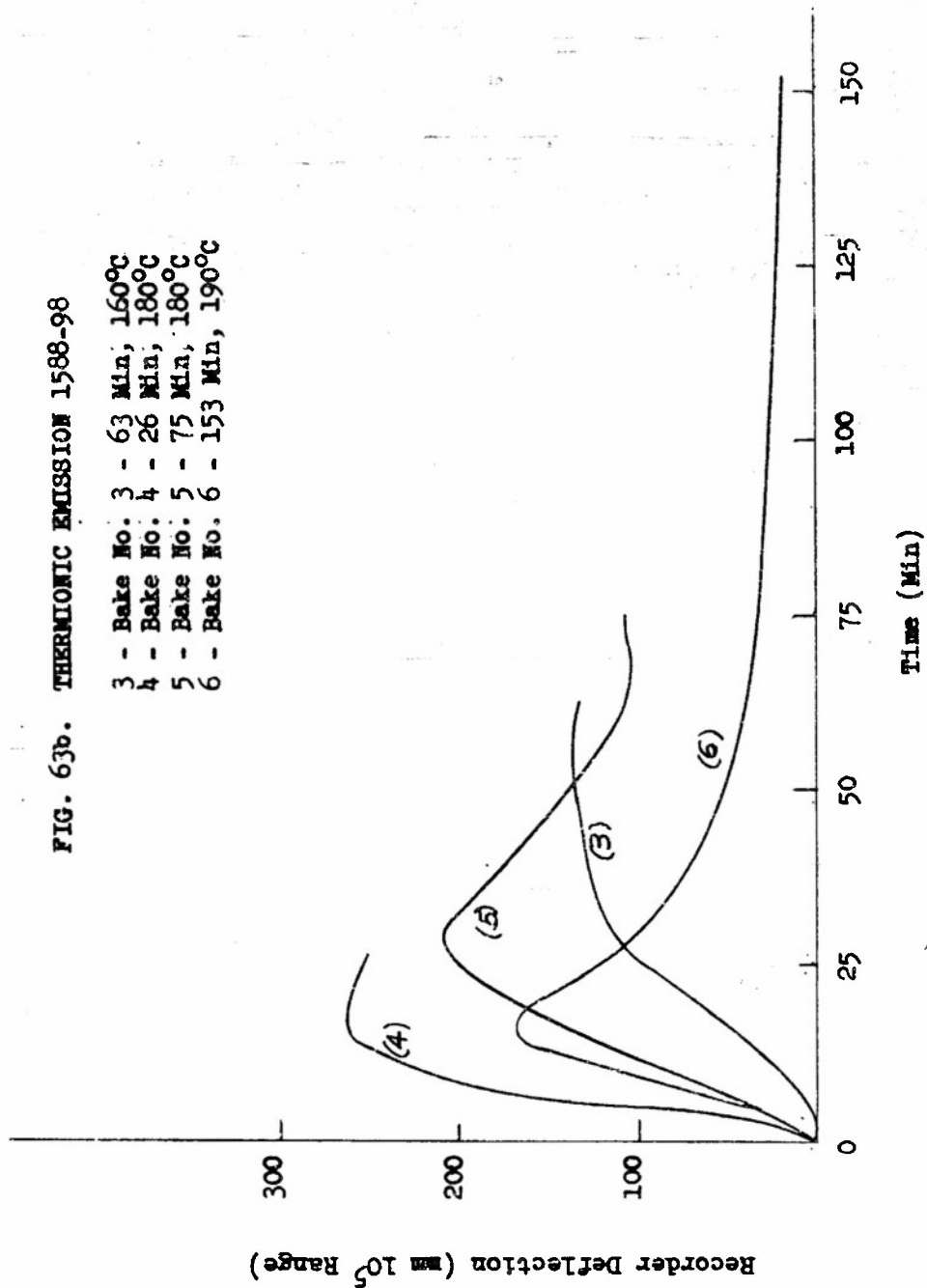
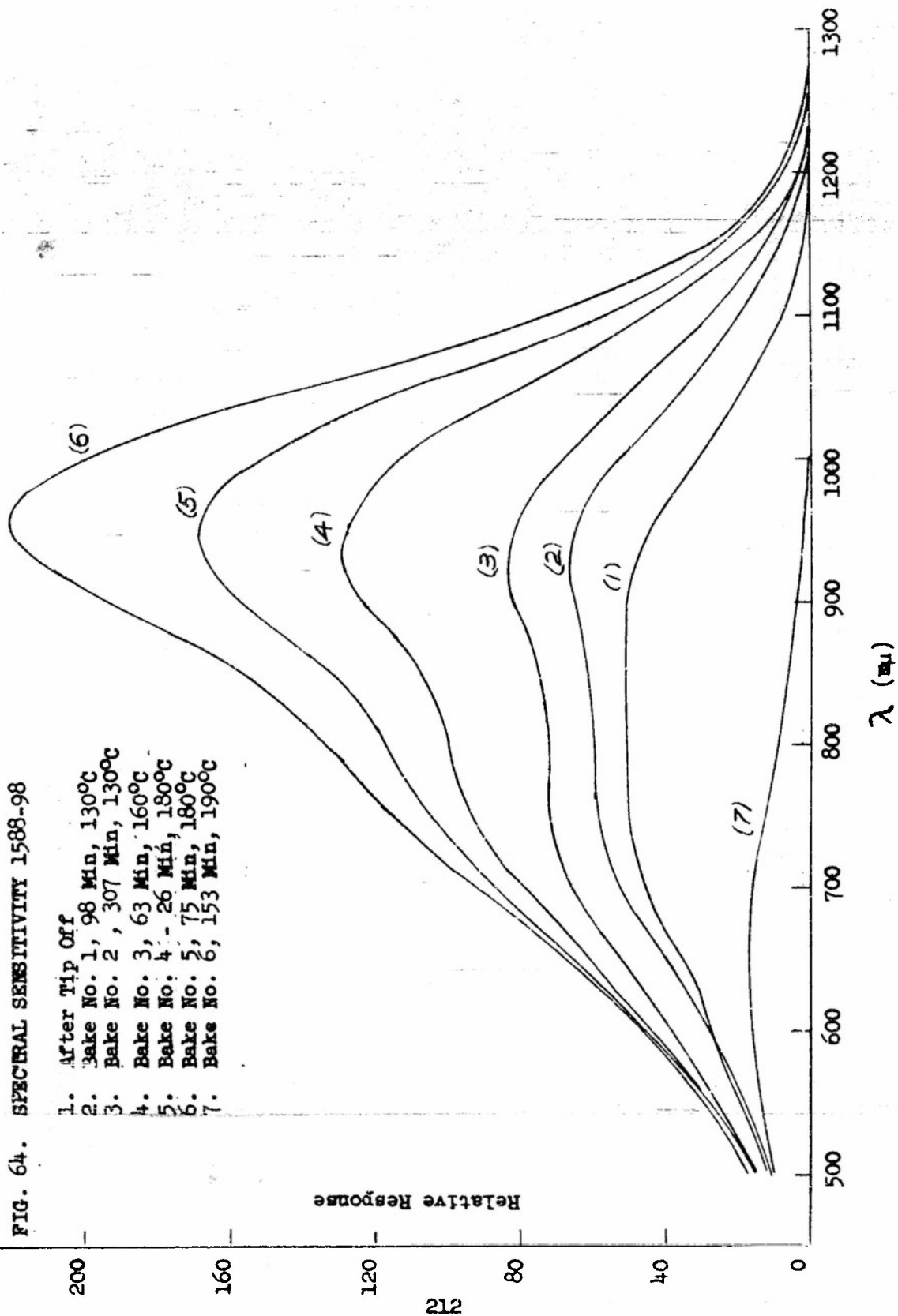


FIG. 64. SPECTRAL SENSITIVITY 1588-98

1. After Tip Off
2. Bake No. 1, 98 Min, 130°C
3. Bake No. 2, 307 Min, 130°C
4. Bake No. 3, 63 Min, 160°C
5. Bake No. 4, 26 Min, 180°C
6. Bake No. 5, 75 Min, 180°C
7. Bake No. 6, 153 Min, 190°C



The final response curve is similar to the curve obtained after extended baking of the cathodes PT1588-93 and PT24C.

The spectral response curves for PT1588-98 scaled to the same photocurrent at 700  $m\mu$  are shown in Fig. 65. The change in the photocurrent during the baking operations relative to the sensitivity after tip off is shown in Fig. 66. From these figures, it is evident that the baking operations not only increased the number of emission centers, but also resulted in the production of new centers which contribute in the long wavelength region beyond 900  $m\mu$ . During the baking operation, the long wavelength limit changed from 930 to 1450  $m\mu$ .

### Discussion.

In considering the significance of the results obtained on the four tubes discussed above we must keep in mind the fact that the cathode, and tube, composition is unknown. Cesium added to each tube reacts, in part, with the cathode, in part with the tube envelope and the remainder is pumped out into the vacuum manifold. How much of the cesium remains on the cathode depends on the rates of the cathode reactions relative to the rates of the other processes. It is quite possible, and likely, that the cathode composition at which maximum thermionic emission is reached depends on the rate of cesium addition. For according to the interpretation of Section 3.1 the amount of cesium in the surface layer depends both on the rate of addition and the rate of the cathode reaction. Thermionic emission is greatly influenced by the amount of cesium in this surface layer. The rate of addition of cesium to the photocathode was much higher for each of the four phototubes discussed above than for the tubes of Section 3.1.

With these facts in mind we now consider the behavior of these tubes in comparison with those of Section 3.1 which were prepared under more carefully controlled conditions. The first observation concerns the behavior of thermionic emission. From Figs. 55, 57, 60, 62 it is evident that immediately after interrupting the flow of cesium the thermionic emission rises, in agreement with the observations of Section 3.1 on the preparation of cathodes at 190°C. However, after halting cesium flow the thermionic emission rose to a maximum and then began to decline rapidly. This is the behavior observed in

FIG. 65. SPECTRAL SENSITIVITY PT1588-98  
CURVES SCALED TO SAME PHOTO-  
CURRENT AT 700 mμ.

1. After Tip Off
2. Bake No. 1, 98 Min, 130°C
3. Bake No. 2, 307 Min, 130°C
4. Bake No. 3, 63 Min, 160°C
5. Bake No. 4, 26 Min, 180°C
6. Bake No. 5, 75 Min, 180°C

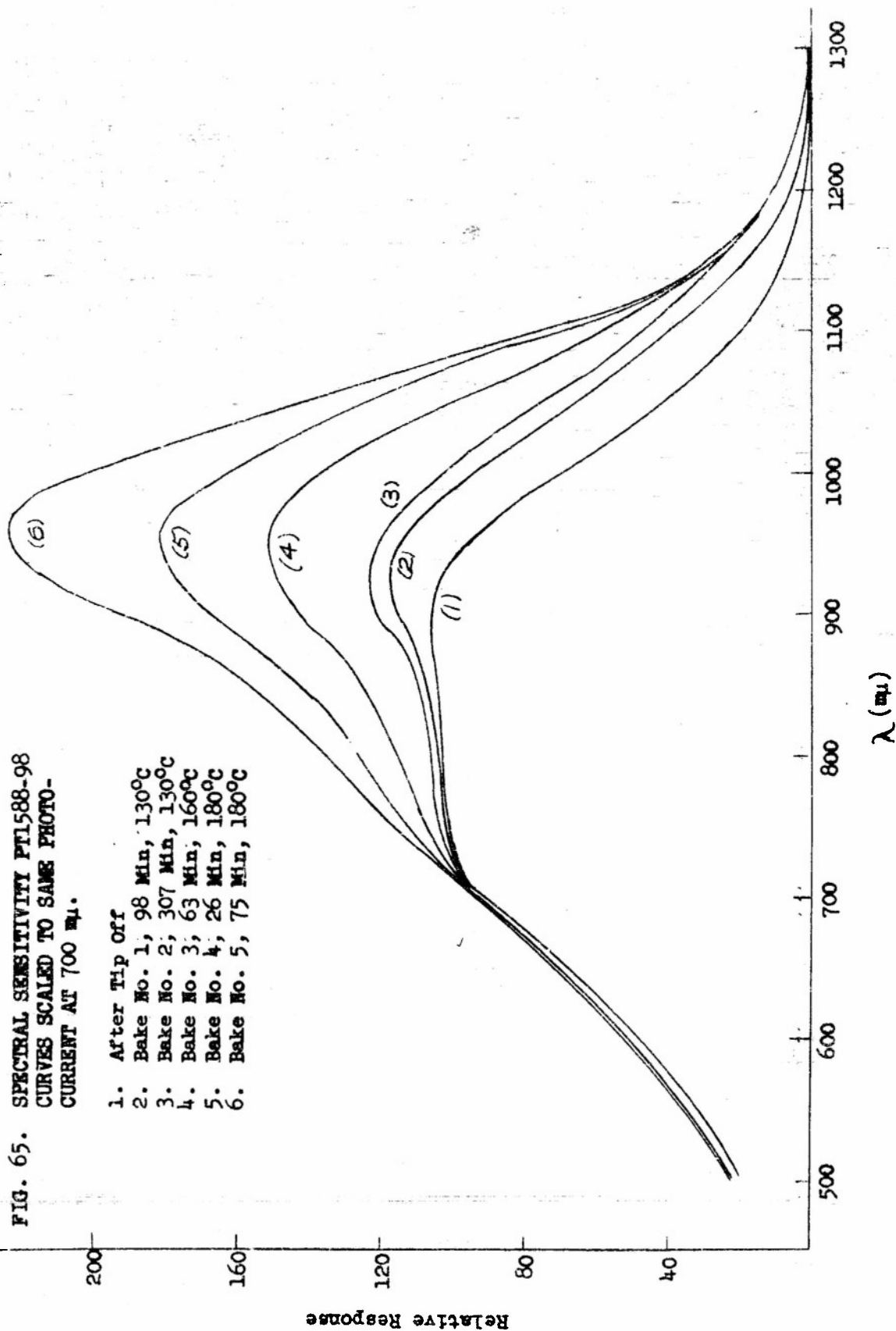
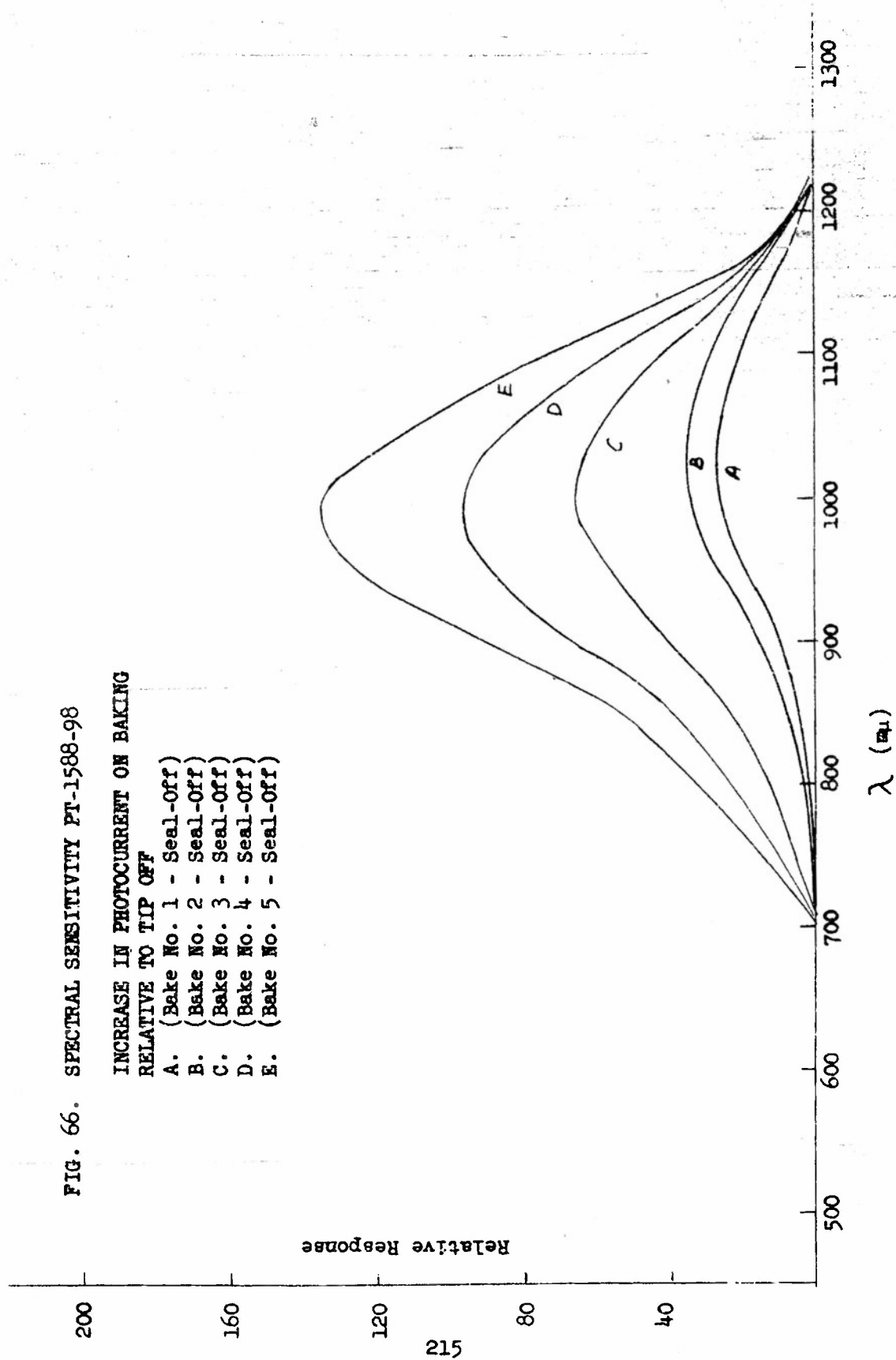


FIG. 66. SPECTRAL SENSITIVITY PT-1588-98

INCREASE IN PHOTOCURRENT ON BAKING  
RELATIVE TO TIP OFF

- A. (Bake No. 1 - Seal-Off)
- B. (Bake No. 2 - Seal-Off)
- C. (Bake No. 3 - Seal-Off)
- D. (Bake No. 4 - Seal-Off)
- E. (Bake No. 5 - Seal-Off)



Section 3.1 for cathodes, prepared at 190°C, before the second maximum in thermionic emission at  $(Cs/O) \approx 1.6$  had been reached. In Section 3.1 the hypothesis was advanced that such tubes contain unreduced silver oxide. If this is correct, then all four of the tubes discussed in the present section behave as though they also contained silver oxide. This is further suggested by the fact that three out of the four tubes showed a pronounced decrease in infrared sensitivity on prolonged baking, sometimes even at rather low temperatures. Moreover, the double maxima obtained in the spectral response curves in several cases are also compatible with a cesium deficiency as pointed out in Section 3.41. On the whole, the data are in fairly good accord with the suggestion that the tubes are cesium deficient and, moreover, that phase equilibrium is far from established in the cathode. This might well be expected because of the high rates of cesium addition employed. These results further suggest that considerable care should be exercised in baking a photocathode prepared in the manner employed in the present section. Moreover, where massive cathodes are being prepared by such methods, some additional cesium should be added when thermionic emission first rises and then falls on halting cesium flow. How far this should be carried can be determined, with a given cesium flow rate, only by trial. The indications are, however, that a more stable cathode can be obtained by means of this procedure. Infrared sensitivity is also likely to be higher. With the discussion of these particular cathodes out of the way we now pass on to a more general consideration of the baking operation.

Indications are strong that the primary function of a baking operation is to remove excess cesium from the cathode. In arriving at this tentative conclusion we have considered not only the data of the present section but also the results of baking a variety of cathodes discussed throughout the report. It must be emphasized that the above statement applies to massive cathodes. In the case of semitransparent cathodes other factors enter, as discussed later. The above view has been stated in several previous sections without a detailed discussion. It seems appropriate therefore to review the evidence which favors it. In considering this evidence it is useful to group the photocathodes to be considered into three groups as follows. (A) Cathodes of the first group are deficient in cesium, i.e.  $(Cs/O) < 2$ , and the cesium deficiency is so great that some cathode constituent remains which is capable of reducing cesium content of the



infrared-sensitive ingredient below that required for maximum sensitivity. It has been proposed tentatively that silver oxide is an ingredient capable of so reducing the cesium content of the infrared-sensitive constituent. (B) Cathodes for which  $(Cs/O) < 2$  but for which the strong oxidizing agent, mentioned in (A), has disappeared. These cathodes contain, however, a milder oxidizing agent (a higher cesium oxide) which is capable of oxidizing excess cesium to  $Cs_2O$ . This is the "regulator" mentioned in Section 3.12. High infrared sensitivity is obtained with this cathode when phase equilibrium is established in the cathode. (C) Cathodes which contain so much excess cesium,  $(Cs/O) > 2$ , that both silver oxide and the "regulating" higher oxide of cesium have reacted completely. Excess cesium can be removed from such cathodes only by reaction with the tube wall, distillation into the vacuum manifold (or a cold trap), or reaction with some tube element other than the cathode. In the case of both of the groups (A) and (B), excess cesium can only be present because a surface coating of cesium has collected at low enough temperature so that the cathode reactions are too slow to remove it. In such cases, warming the tube to a relatively low temperature for a short period of time is sufficient to remove the excess. If the cathode belongs to group (B) not much care need be taken in the baking operation and temperatures up to at least  $190^{\circ}C$  can be used for moderate periods since cathode equilibrium seems to be established. Excessively prolonged heating may, however, result in a drop in sensitivity due to reaction with the tube envelope. Examples of the effect of baking cathodes of group (B), containing excess cesium, for short periods are given in Section 3.41. Examples showing the results of baking cathodes of group (A) for short periods at  $190^{\circ}C$  are given in Section 3.12. The cathodes of the present section also probably belong to group (A) and contain slight amounts of surface excess cesium which distills onto the cathode on sealing off the cesium source. An example of a massive cathode of type (C) has already been discussed in Section 3.32. An even more striking example is discussed in Section 4.23. It may be very difficult to remove excess cesium from a cathode of type (C) but it will usually be possible to do so since a volatile oxide of cesium is formed when the composition is such that  $(Cs/O) > 2$  (see Section 4.1). There is usually some tube element which is reactive enough to remove this oxide from the cathode. It is to be noted, however, that oxygen is also removed in this case. Moreover, the rate of removal may well be variable and dependent on the extent to which tube elements

have already been saturated with cesium. For cathodes of types (A) and (B) the amount of excess cesium is usually small if normal processing methods have been used. In the case of cathodes of type (C), however, large excesses may be present depending on the amount of cesium added. It may also be necessary to use rather high baking temperatures. Using these three classifications it is usually possible to understand the results of a baking operation on a massive cathode although the effect cannot be predicted unless the cathode composition and the manner of preparation are known.

In the above discussion great emphasis has been placed on removal of excess cesium by baking and there can be no doubt about the importance of this factor. Other changes do occur, however, in prolonged baking of a photocathode. These changes include the removal of oxygen in the case of type (C) cathodes and grain growth of both metallic silver and cesium oxides undoubtedly occurs. In the case of massive cathodes it has not proved necessary to invoke these factors to account for large changes in infrared sensitivity on baking. Since, however, both metallic silver and  $\text{Cs}_2\text{O}$  seem to be involved in producing infrared sensitivity, grain growth probably has an influence even though we have not been able to clearly demonstrate it. We believe that cesium content is a major factor, however, because the observations of Section 3.12 show that cathodes prepared at  $190^\circ\text{C}$  can lose sensitivity on halting cesium flow at small (Cs/O) ratios and sensitivity is restored on resuming cesium addition. Moreover, for cathode PT24C of Section 3.2 infrared sensitivity is partially restored by adding cesium after prolonged baking had destroyed the infrared response. The fact that infrared sensitivity is only partially restored for PT24C can be accounted for in a variety of ways as discussed in Section 3.25.

### 3.5 Effect of Silver Base on Photoelectric Emission

Two cases have been encountered in which a pronounced effect of silver base on photoelectric emission is observed. In the first of these cases the effect was unexpected and arose during the study of cathode composition using a radioactive cesium tracer. The results are described in Section 3.51. In the second case an attempt was made to systematically investigate the effect of varying the thickness of silver base by preparing cathodes on silver film bases of

graded thickness. This investigation was not continued systematically to a conclusion because the first results indicated that further studies of the baking process and of cathode composition were required before the results of such a study could be properly interpreted. The preliminary results are of some interest, however, and are reported in Section 3.52.

### 3.51 Thick evaporated silver films

The cathode used in the composition study was prepared on a base consisting of a thick evaporated silver film deposited on a microscope cover glass substrate (see Section 2.4). With this tube design (Fig. 14) it was expected that a typical massive cathode would be formed. This did not prove to be entirely correct.

The results of the tracer study are discussed in Section 4.1. The effect of silver film thickness seems important enough, however, to justify discussion in a separate section. The reasons are as follows. Much of the material discussed in preceding sections was collected before the tracer study was begun. As the result of this work the hypothesis was formed that infrared sensitivity depended mainly on the cesium to oxygen ratio and equilibration of the cathode by baking so as to remove excess cesium. Although we knew that silver played a role in cathode sensitivity, nevertheless the consistent and apparently understandable results obtained with massive cathodes tended to obscure the important role played by silver. The difficulties encountered in the preparation of semitransparent cathodes were regarded as due, in all probability, to lack of control in the cesium addition step and to the fact that a fifty-percent transmission silver film is one in which grain contact is likely to be poor. In order to avoid the technical difficulties introduced by this latter factor the tracer tubes were prepared on such thick silver films that grain contact could not be a problem. In performing the experiments, however, the important role of silver in the cathode was forcibly demonstrated. It was found that a step performed at the very beginning of the cathode preparation could so determine the character of the cathode that no intermediate operation which we tried could produce an infrared-sensitive cathode except in a few, apparently accidental, cases. The demonstration is apparently conclusive. In a number of cases both thermionic and photoelectric emission were followed out to (Cs/O) ratios as high as 10 without any

indication of high infrared sensitivity. The behavior of thermionic and photoelectric emission was entirely different from that described in Section 3.1 as long as silver films of 10,000A thickness were used. Typical results are described below but it seems worthwhile to again emphasize here the conclusive nature of the results. The fact that an operation at the very beginning of the cathode preparation influence the outcome is established beyond reasonable doubt since a considerable number of tubes were prepared each of which was followed throughout the intermediate stages. Moreover, the composition of the cathode was determined in several cases using radioactive cesium tracers and it is established that the (Cs/O) ratio is not the determining factor since in subsequent experiments, using thick films, good infrared sensitivity was obtained at nearly the same (Cs/O) ratio as those for which poor tubes were obtained using thinner films. Typical examples are described below.

During the early stages of the tracer study the evaporated silver surface was formed by the deposition of a layer approximately 10,000A thick in 15 minutes. During the fabrication of a series of tubes using this surface very irreproducible results were obtained. In a series of 14 tubes only two cathodes were obtained which could be considered as having good infrared sensitivity.

During the fabrication of these poor cathodes the thermionic and photoelectric emission did not follow the normal behavior for massive cathodes.

The behavior of the poor cathodes prepared on 10,000A silver bases is illustrated by the behavior of PT659-42. During the glow discharge oxidation  $13.2 \times 10^{-7}$  gramatoms of oxygen were deposited to give a uniform second order yellow-green oxide film. The tube current data for this cathode are shown in Fig. 67 and the photoelectric emission during cesium addition in Fig. 68. During the cesium addition to this tube there was actually no appreciable thermionic emission. The very small observed current (Fig. 67) is typical of an ohmic conduction current flowing between the electrodes. The cathode developed a large  $F_1$  response without appreciable  $F_2$  as shown in Fig. 68. On cooling the cesium source the conduction current decreased rapidly but the  $F_1$  response did not change appreciably. Finally, corresponding to a rapid growth in the conduction current at approximately 160 minutes there was a decrease in the  $F_1$  response. Cooling the cesium source at 176 minutes resulted in a decrease in the conduction current and an increase in the  $F_1$  photoemission. In addition a small infrared response appeared which disappeared on cooling the tube as shown by

FIG. 67. THERMIONIC EMISSION  
DURING CESIUM ADDITION  
PT-659-42

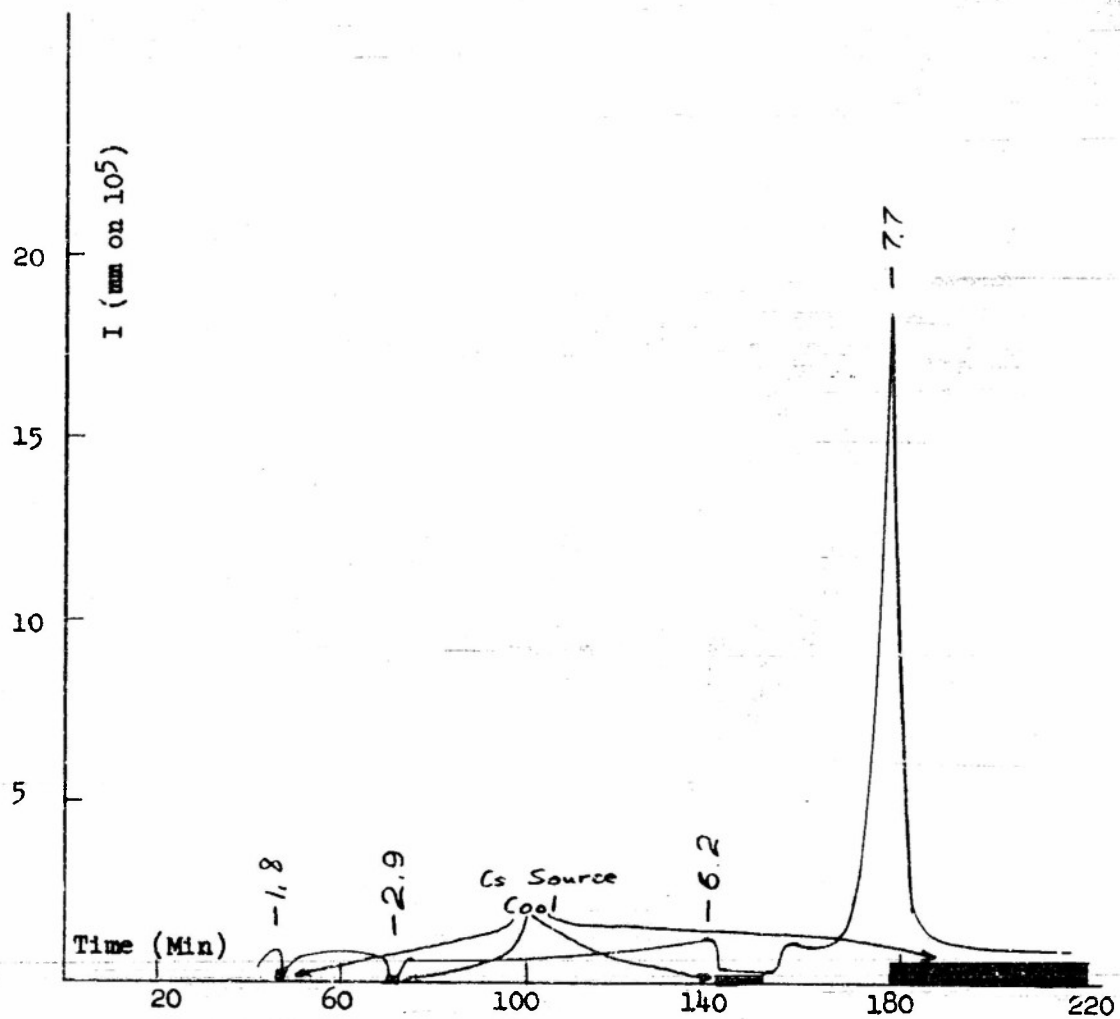
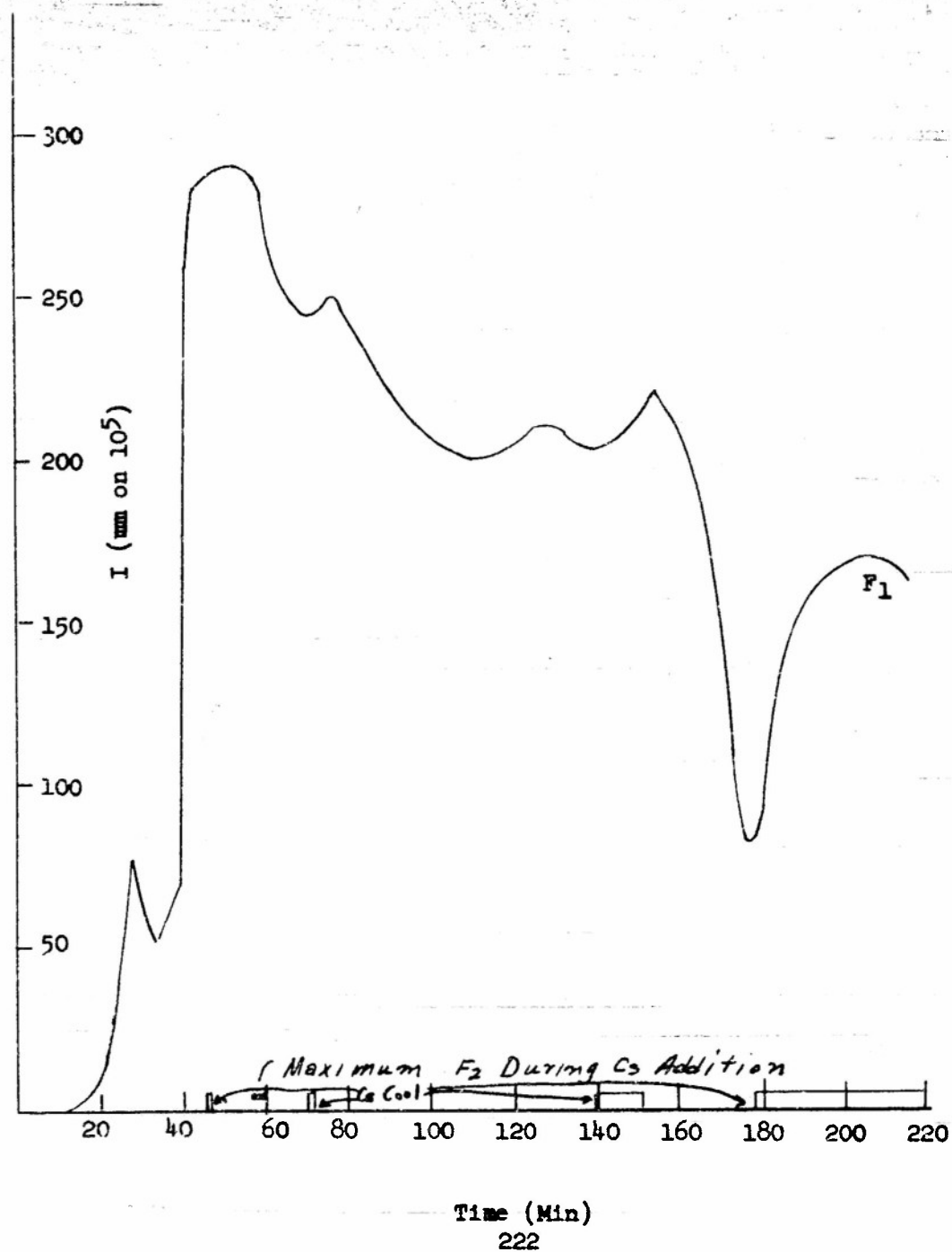


FIG. 68. OVEN SPECTRAL DATA  
FOR PT-659-42





the following data:

	Response after cooling cesium source	Response after cooling tube
F <sub>1</sub>	167 mm(10 <sup>5</sup> range)	158 mm(10 <sup>5</sup> range)
F <sub>2</sub>	83	47
F <sub>3</sub>	1	0
F <sub>4</sub>	1	0
F <sub>5</sub>	0.2	0

These data suggest a long wavelength limit in the neighborhood of 900  $\mu$  before cooling the tube, a long wavelength limit near 800  $\mu$  after cooling the tube. The spectral response for PT659-42 after sealing off the cesium source is shown in Fig. 69. It is to be noted that the photo-sensitivity of the final cathode is very low. In general, the spectral response curves for the finished cathodes prepared on 10,000A silver films were quite variable. In several instances appreciable excess cesium was introduced and on baking the cathode at 130°C surfaces were obtained which had maxima at 600 - 700  $\mu$  with long wavelength limits from 800 to 1000  $\mu$ . During cesium addition, the absence of thermionic emission assured that the final cathode would not have appreciable infrared sensitivity. It must be emphasized that excess cesium was not responsible for low infrared sensitivity. The tubes, like PT659-42, did not develop infrared response at any intermediate stage and extended baking did not lead to infrared sensitivity for the final photocathode.

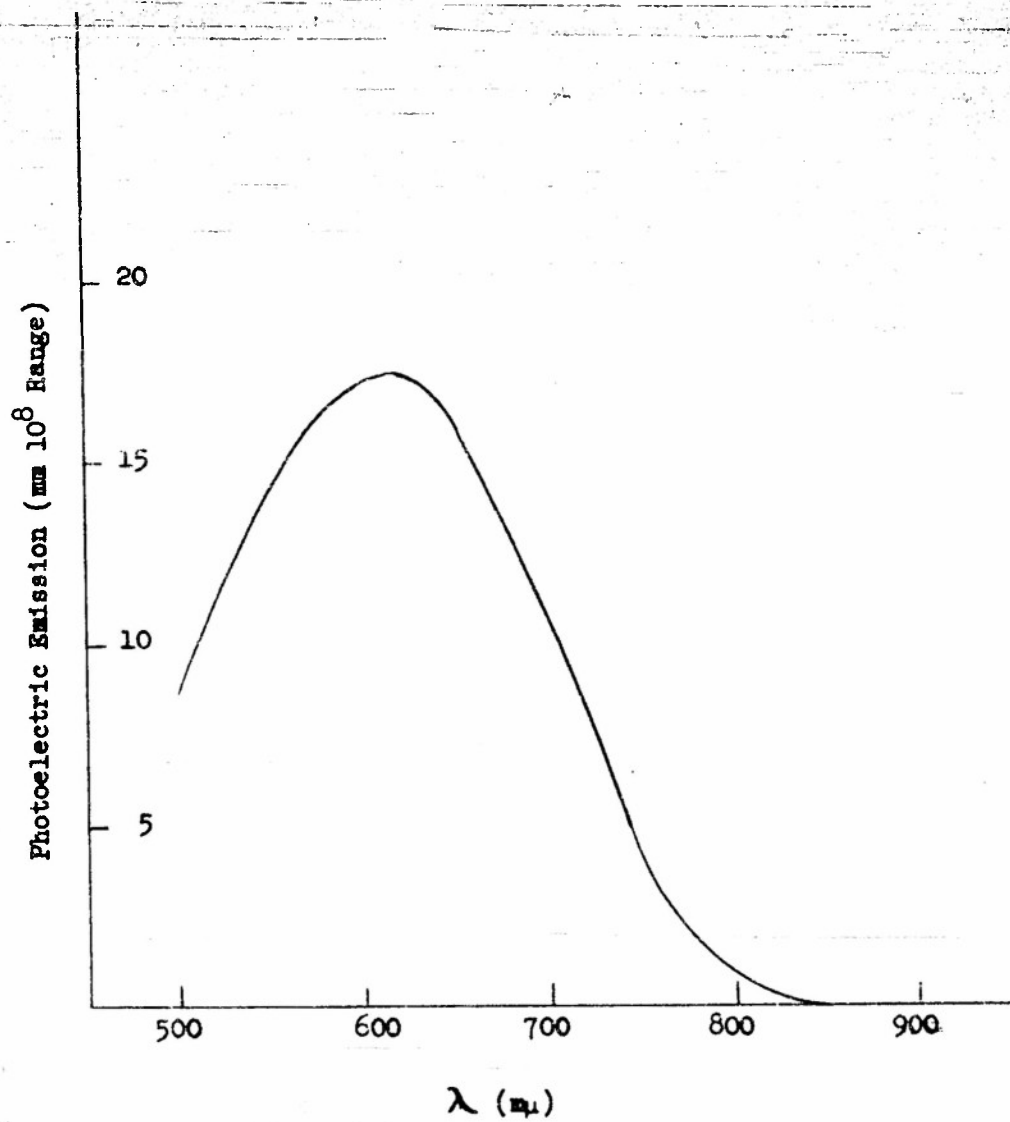
After considerable experimentation, in which possible sources of the difficulties were eliminated, the conclusion was reached that the troubles must rise from characteristics of the silver film and its oxidation. Consequently several cathodes were prepared in which the silver film thickness was increased several fold. During the fabrication of these cathodes the normal massive cathode behavior was observed, i.e. thermionic emission increased on cooling the cesium source and infrared emission increased on cooling the tube. Typical of the spectral responses of these tubes are the following:

Tube	Max. PE $\lambda$	Long $\lambda$ limit	1/2 Max. PE $\lambda$
PT1588-122	950	1350	1080
PT1588-130	920	1250	1020

Subsequent tubes prepared using the thicker silver films (20,000 to 40,000A) consistently exhibited a normal behavior during fabrication.



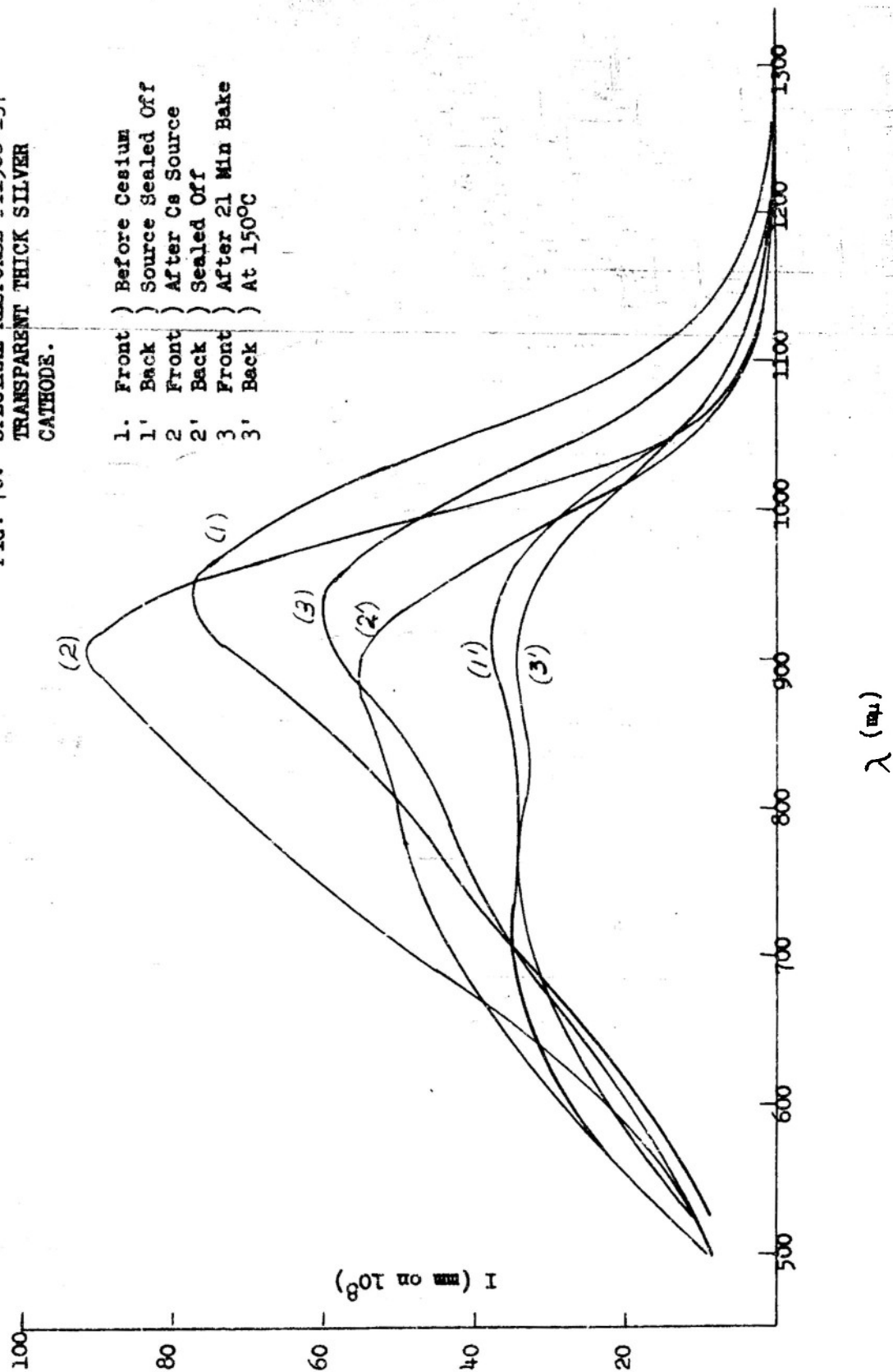
FIG. 69. SPECTRAL RESPONSE FOR  
PT-659-42 AFTER CESIUM  
SOURCE SEALED OFF.



As discussed in Part I of this Final Report Series the structure of evaporated silver films depends very markedly on the evaporation rate as well as heat treatment conditions. As the rate of evaporation is decreased the grain size of silver increases in a manner similar to that occurring during heat treatment. Consequently a cathode, PT1588-137, was prepared in which a 6000A silver film was formed by a 10 hour evaporation compared to the 15 minute 10,000A film used in the poor tubes. During the processing of this tube the emissive properties behaved in a normal manner. The spectral response of this cathode is particularly interesting since the final surface was quite transparent. As shown in Fig. 70 the cathode after fabrication and bake exhibited on front illumination a spectral response typical of good massive cathode tubes. On back illumination, however, the spectral response curve exhibits two peaks, one at approximately 750 m $\mu$  and a second near 920 m $\mu$ . In addition there is a marked reduction in infrared response. Considering the thickness of the initial silver layer (about sixty times greater than for normal semitransparent cathode) it is, however, surprising that a more marked difference in response did not occur. The back illumination responses are similar to those for frontal illumination of PT24C during the initial development of photoemission and during the final stages of decay by extended baking of the good infrared-sensitive photosurface, (see Section 3.2).

These results were briefly discussed in Part I of this Final Report Series. As was pointed out there the silver film thickness, 10,000A, greatly exceeds the critical thickness at which silver grain merging takes place. We can make only one addition to the discussion of Part I. We have already referred, in Section 1.6, to the work of Kluge on photocathodes prepared on specular silver bases (thick evaporated silver films). In later work Kluge<sup>26</sup> discovered that on replacing a specular reflecting silver base by a roughened silver base the integral sensitivity is increased and, moreover, the long wave maximum in spectral yield shifts toward the infrared by more than 100 m $\mu$ . We suspect that this result of Kluge is related to our observations outlined above. In the normal preparation of massive cathodes (see Section 2.31) the silver base is roughened by means of a nitric acid etch before oxidation. In the preparation of cathodes for the tracer experiments the nitric acid etch was not used since we did not wish to complicate the composition determination by the addition of a new variable. Instead

FIG. 70. SPECTRAL RESPONSE PTL588-137  
TRANSPARENT THICK SILVER  
CATHODE.



of a nitric acid etch the repeated oxidation and thermal decomposition cycle served to roughen the surface. With 10,000A silver films this was not, however, sufficient to insure obtaining a highly infrared-sensitive cathode although with thicker films infrared-sensitive cathodes could readily be made. The precise connection with Kluge's work is not clear but it seems possible that the two phenomena are related. Kluge's hypothesis that roughening increases infrared sensitivity because a higher surface area creates more active centers for cesium adsorption (de Boer's theory) seems to us to be too simple. On reconsidering the problem since Part I was written one additional fact has become evident. We have had far better success with the preparation of photocathodes which do not rest on a glass substrate. It seems quite possible that some chemical reaction with glass, or some impurity occluded in glass, could account for these troubles. It would be worthwhile to alter the nature of the substrate at first perhaps by rigorous chemical cleaning methods followed by extended outgassing. It would also be worthwhile to pretreat the envelope with cesium before evaporating a silver film so as to saturate the glass with cesium. This suggestion is along the same line as those made in Part I although somewhat more specific. Until these possibilities have been explored nothing definite can be said as to the reasons for the observations. There is, however, every reason to believe that  $\text{Cs}_2\text{O}$  is formed in all of the photocathodes whether they are highly infrared-sensitive or not and hence the presence of  $\text{Cs}_2\text{O}$  is not in itself sufficient to insure high infrared sensitivity.

### 3.52 Evaporated silver wedge cathodes

The procedures used in the fabrication of the two wedge cathode tubes have been described in Section 2.32. The results obtained with these cathodes are described below.

During the fabrication of PT31 and PT32 the cesium addition was not sufficiently well controlled and consequently excess cesium was introduced into the tubes. The tubes were provided with a dry ice-acetone trap which was maintained cold during the baking operations and spectral response measurements. At the time these tubes were prepared the effect of excess cesium on the photo-emission characteristics had not been worked out. The spectral responses were measured using the following conditions: lamp - 5.0 volts, slit 0.2 mm, collector

voltage - 6.5 volts and low electrometer sensitivity. The spectral response maxima wavelengths and long wavelength limits are shown in Table XIII. In this table, and in the subsequent figures, the position in centimeters gives the point at which the measurement was made. These are distances measured parallel to the film surface. The film thickness is highest when the position in centimeters is highest. The original silver film has a transmission of 50% at a position of 2 cm.

The spectral distributions for these cathodes were defined by the distance in centimeters from the open end of the gold contact surface. The spectral data for PT31W after tip off and the first bake (160°C) are shown in Figs. 71 and 72. For PT31W the maximum sensitivity after tip off occurred at 2.0 cm, the region corresponding initially to 50% transmission. After baking at 160°C for 1 hour the maximum sensitivity moved to 2.5 cm and there was an overall decrease in photoemission as shown. In Table XIII it is interesting to note that during the processing operations there was no marked difference in response of the cathode as a function of position. Furthermore it may be noted that under the fabrication conditions used it would be difficult to remove excess cesium from a phase having a relatively low cesium vapor pressure. Actually extensive baking of this type of surface produces a continuous decline in the photoresponse over all wavelengths. The precise reason for this is not known. It would not, however, be surprising if the effects were related to reaction of the cesium oxide with the glass surface.

The spectral data for PT32W after tip off, the first two bakes, the silver evaporation, and the following two bakes are shown in Figs. 73 through 78.

Several observations made during the fabrication of this cathode are of interest. As shown in Fig. 73 the surface after fabrication had a maximum sensitivity at 2.0 cm the maximum emission wavelength being 700  $m\mu$  and the long wavelength limit 1100  $m\mu$ . On baking the cathode the differences in sensitivity at 2 - 3.5 cm and at wavelengths longer than 800  $m\mu$  became less marked (see Fig. 74). After a second bake at 125°C the surface exhibited the variety of responses shown in Fig. 75. For the 3.5 and 5.0 cm positions there was an appreciable increase in the infrared response while the 2.0 and 2.5 cm positions lost sensitivity. At this stage the spectral responses are somewhat similar to those obtained by Morozov and Butslov<sup>24</sup>.

TABLE XIII. PROCESSING DATA FOR PT31W AND PT32W

Tube	Processing Condition Distance (cm) from thin end of wedge.	Spectral Response Maxima (mμ)					Long Wavelength Limit (mμ)						
		1.5	2.0	2.5	3.0	3.5	5.0	1.5	2.0	2.5	3.0	3.5	5.0
PT31W													
	After tip off												
	Bake No. 1.1 hr., 160°C	650	695	695	655	640		1000	1090	1030	1000	950	
	trap cold	650	650	660	660	625		900	1000	1000	1000	950	
	Bake No. 2.1 hr., 140°C												
	trap cold	645	650	650	640	625		900	1000	1000	930	900	
	16 hr. later,												
	trap at 280°C	620	655	660	625			900	950	930	860		
	Bake No. 3. cesium ad-												
	dition. 10 min, 130°C	590	600	630	625	590		775	820	830	830	775	
	Bake No. 4. cesium ad-												
	dition. 15 min, 130°C	530	552	550	550			650	675	675	575		
	Bake No. 5. 78 min,												
	160°C, trap cold	625	630	650	600			850	950	980	830		
PT32W													
	After tip off												
A.	Bake No. 1. 25 min	640	700	700	700	700	630	1100	1100	1100	1050	1050	1050
B.	1250°C, trap cold	675	710	715	740	750	730	1050	1100	1100	1100	1080	1050
C.	Bake No. 2. 25 min												
	1250°C, trap cold	680	660	660	675	725	750	975	1050	1050	1050	1100	1100
D.	Ag evaporation												
	trap cold	580	625	625	615	640	625	850	900	900	900	910	900
E.	Bake No. 3. 75 min												
	1250°C, trap cold	630	635	640	640	650	625	925	925	925	930	930	900

TABLE XIII. (Continued)

Tube	Spectral Response						Long Wavelength					
Processing Condition	Maxima (m $\mu$ )						Limit (m $\mu$ )					
Distance (cm) from thin end of wedge.	1.5	2.0	2.5	3.0	3.5	5.0	1.5	2.0	2.5	3.0	3.5	5.0
F. Bake No. 4. 200 min												
152°C, trap cold*	670	675	675	680	675	660	1000	1000	1000	1000	1000	950
G. 48 hrs. later	665	665	665	665	665	655	1000	950	930	900	950	900
H. Bake No. 5. 60 min												
150°C	640	-	660	-	655	-	1000	-	970	-	900	-
I. Bake No. 6. 45 min												
180°C	650	665	665	665	665	650	950	950	950	950	950	950

\* Trap at room temperature 16 hours before response measurement.



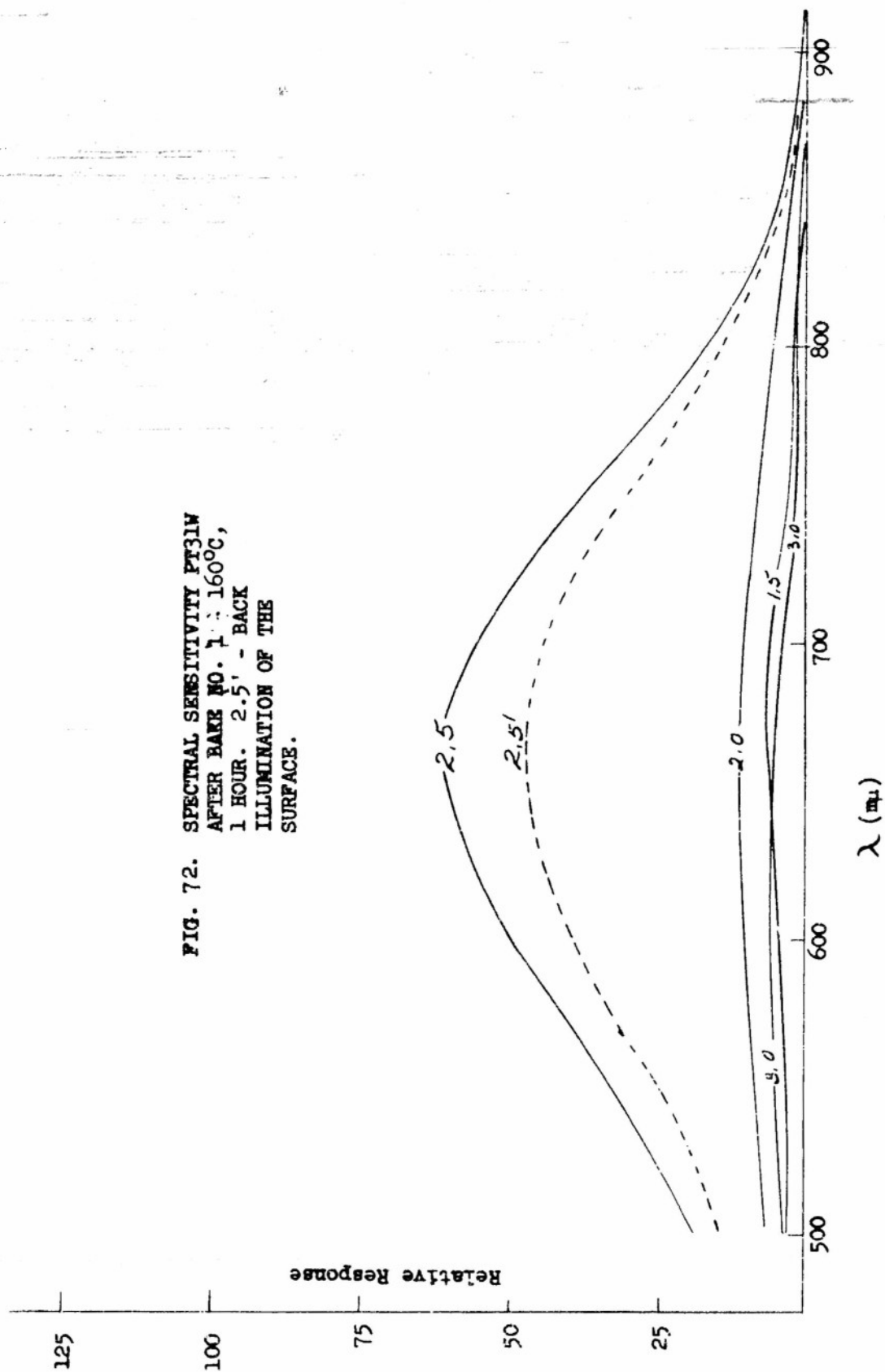


FIG. 71. SPECTRAL SENSITIVITY PT31W  
AFTER FABRICATION.

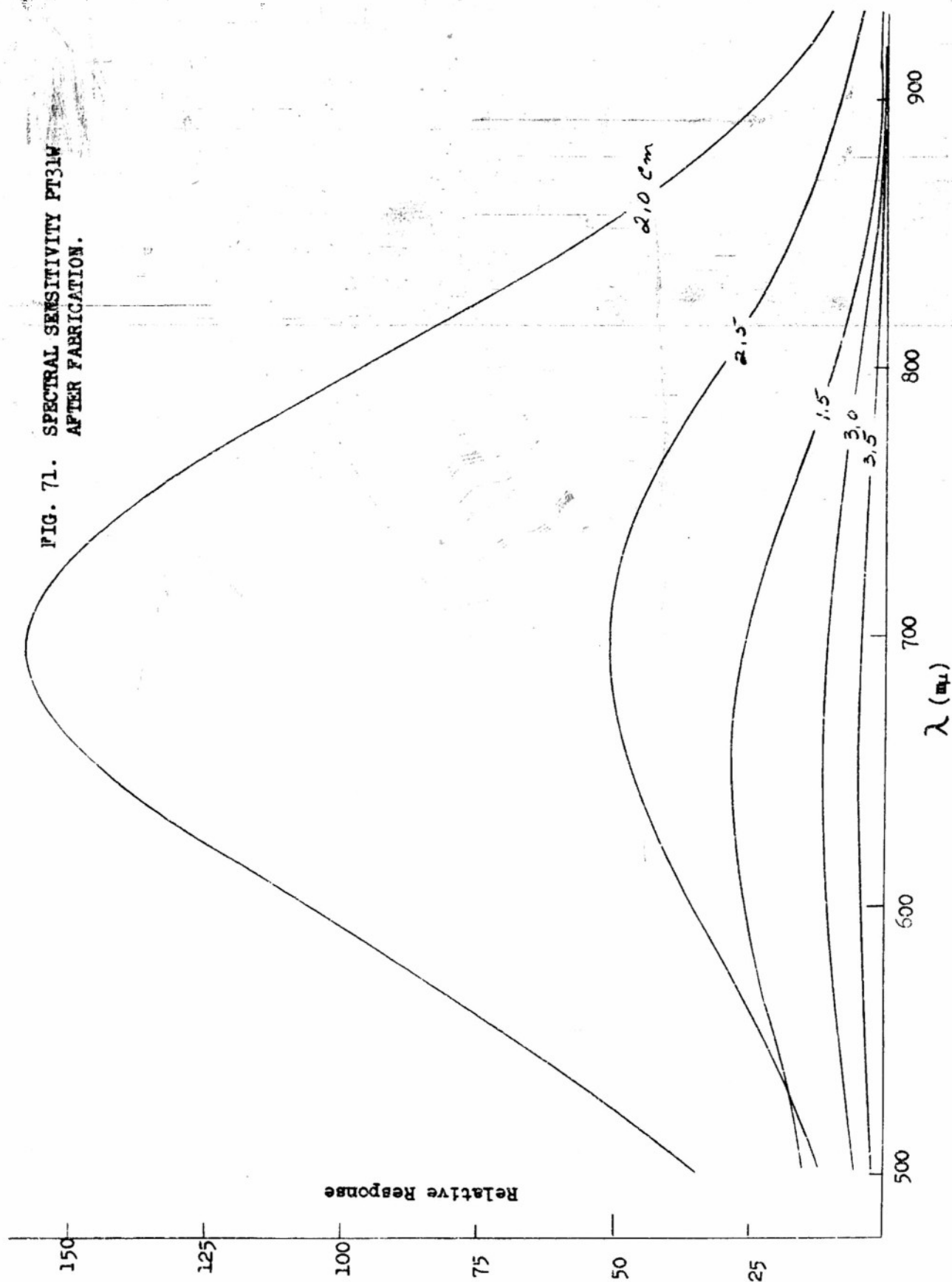


FIG. 73. SPECTRAL SENSITIVITY PT32W  
AFTER TIP OFF

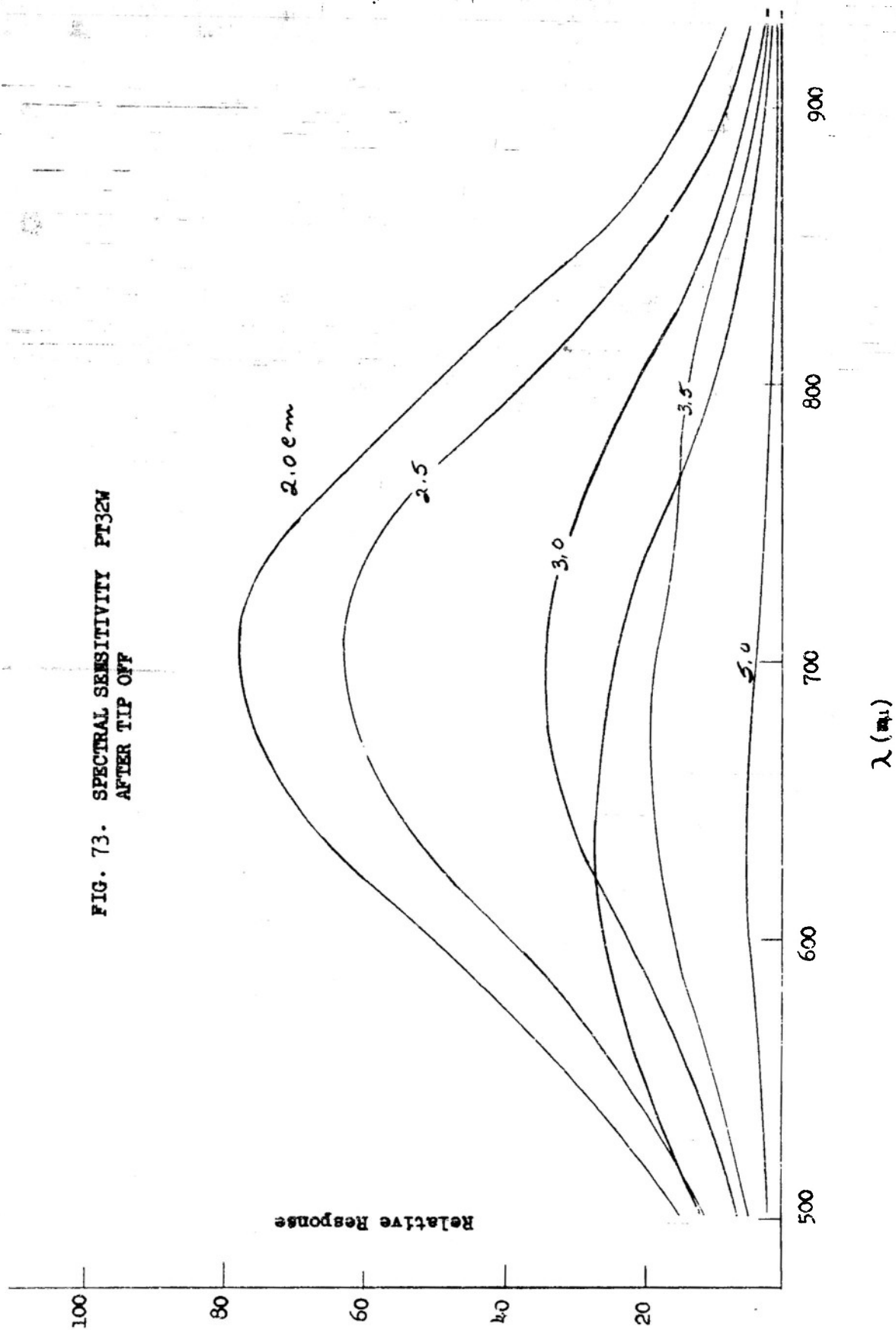


FIG. 74. SPECTRAL SENSITIVITY PT32W  
AFTER 1<sup>st</sup> BAKE 125°C - 25 MIN.

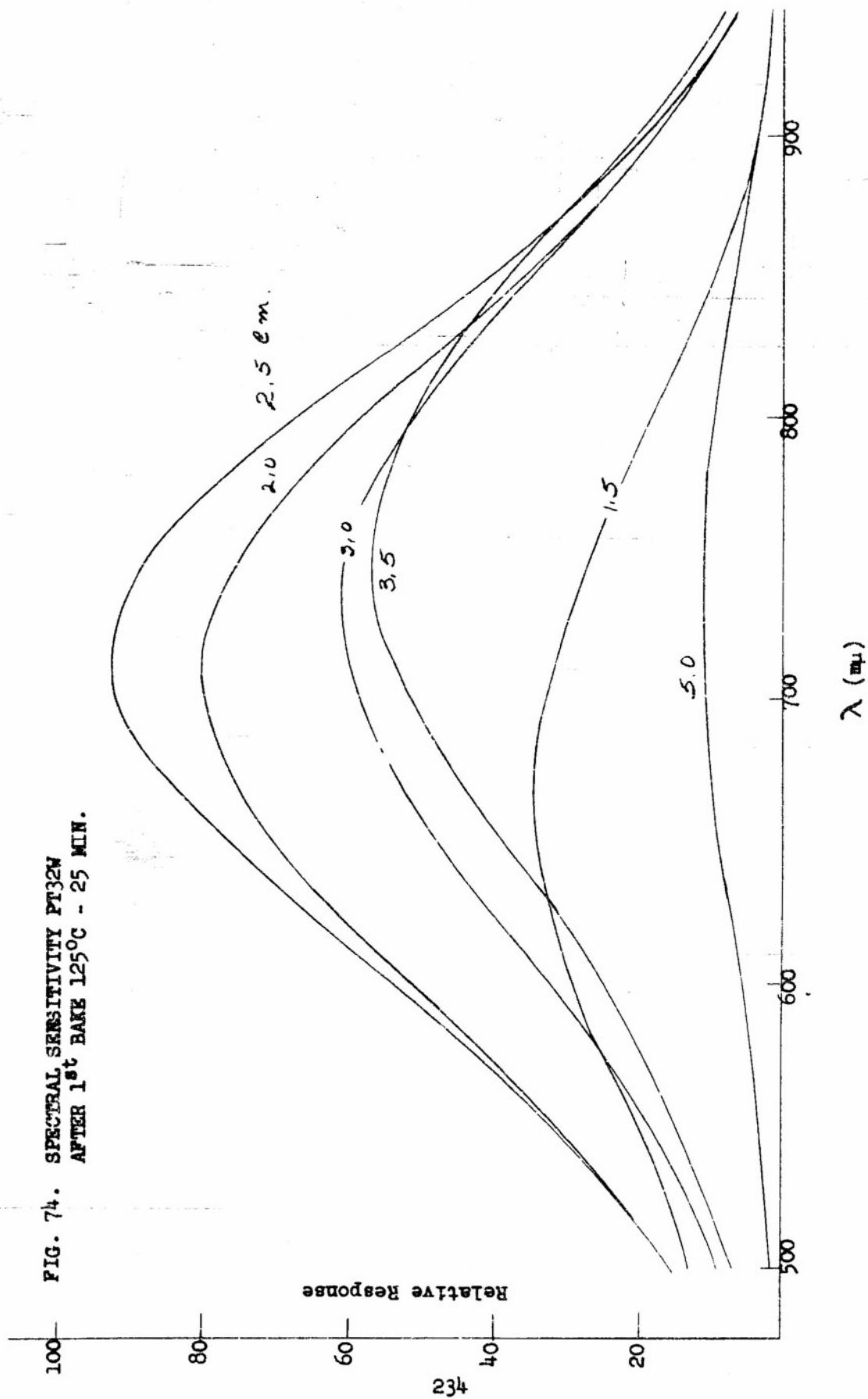


FIG. 75. SPECTRAL SENSITIVITY PT32W  
AFTER 2<sup>nd</sup> BAKE 125°C - 25 MIN.

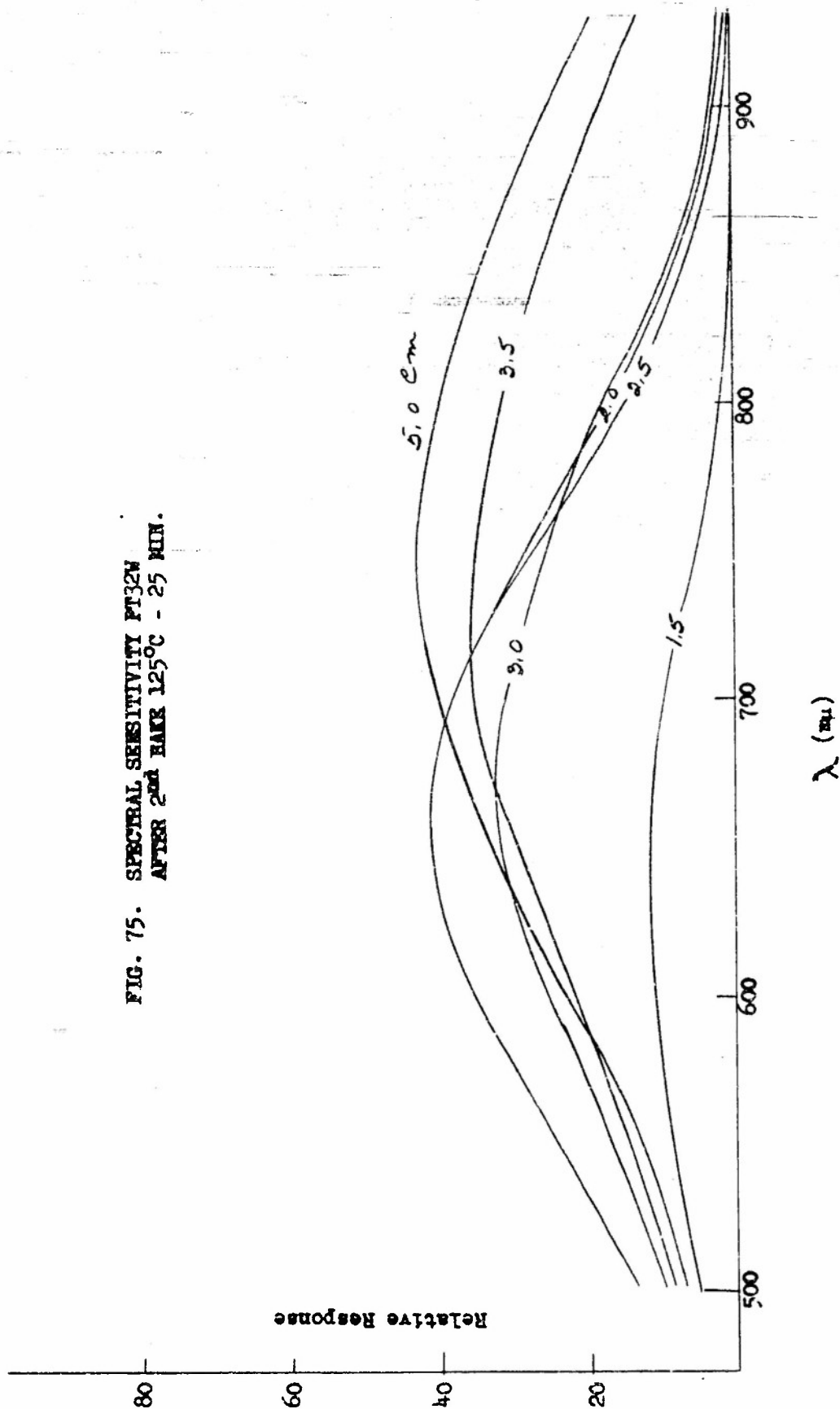
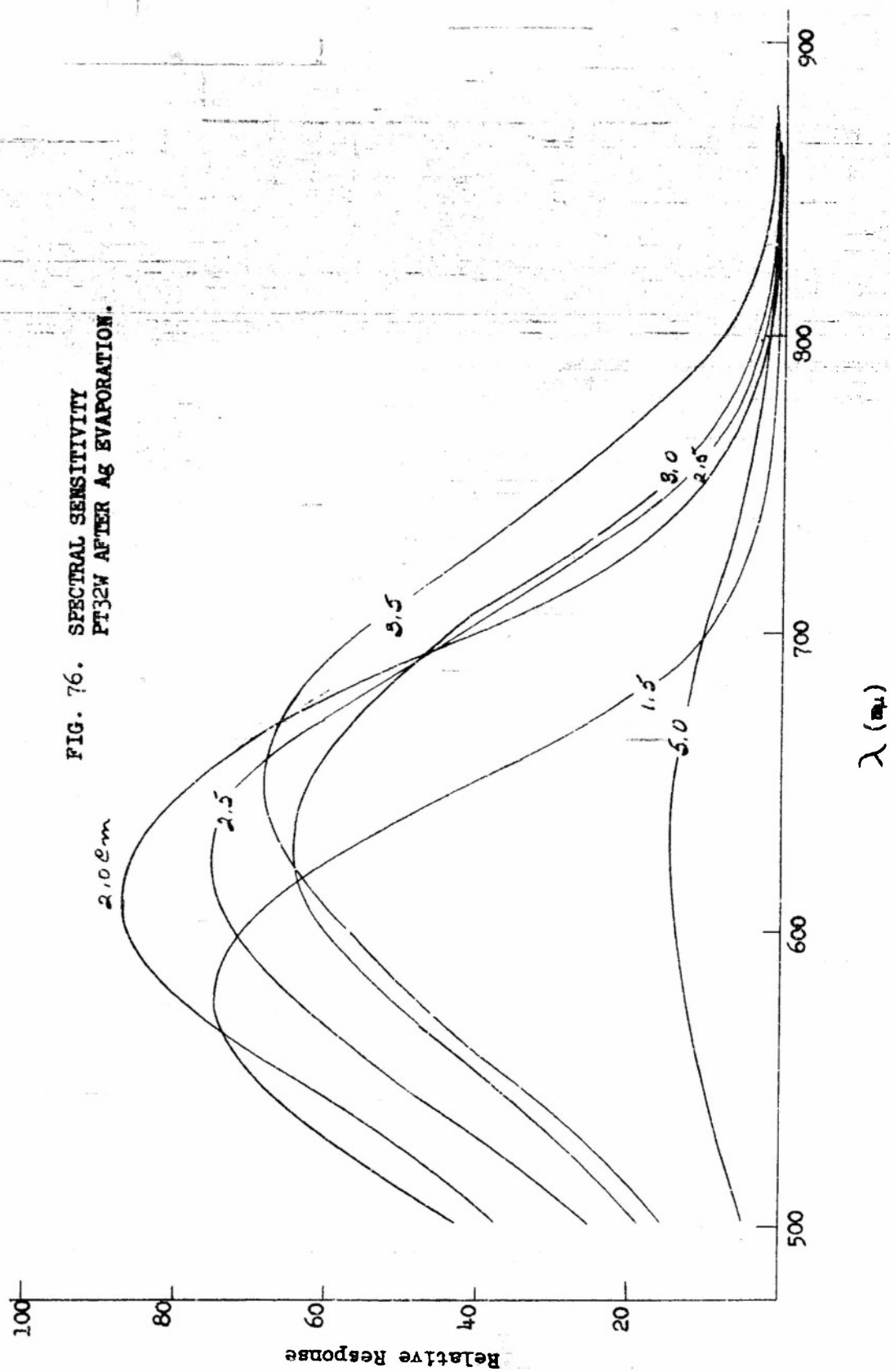


FIG. 76. SPECTRAL SENSITIVITY  
PT32W AFTER Ag EVAPORATION.



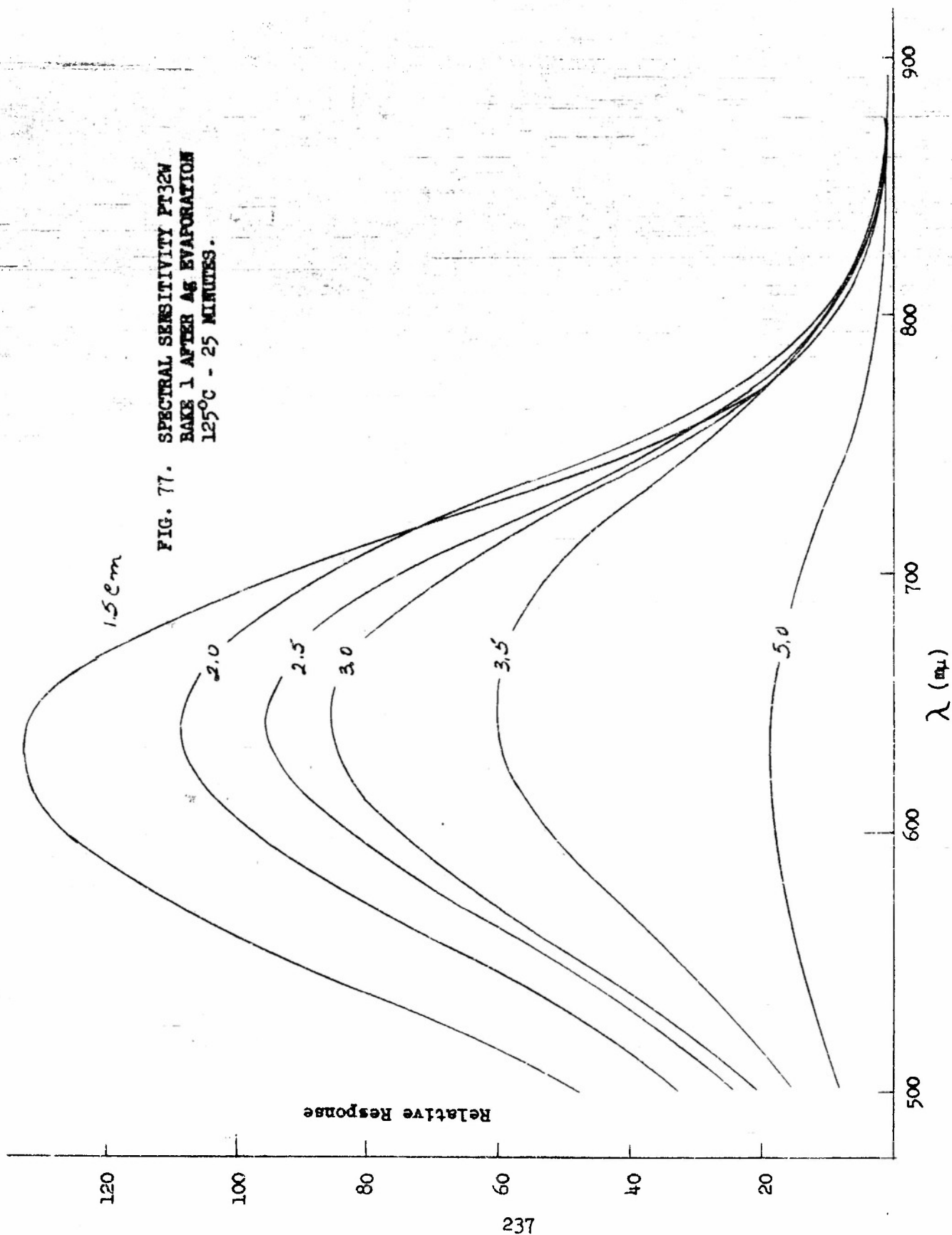
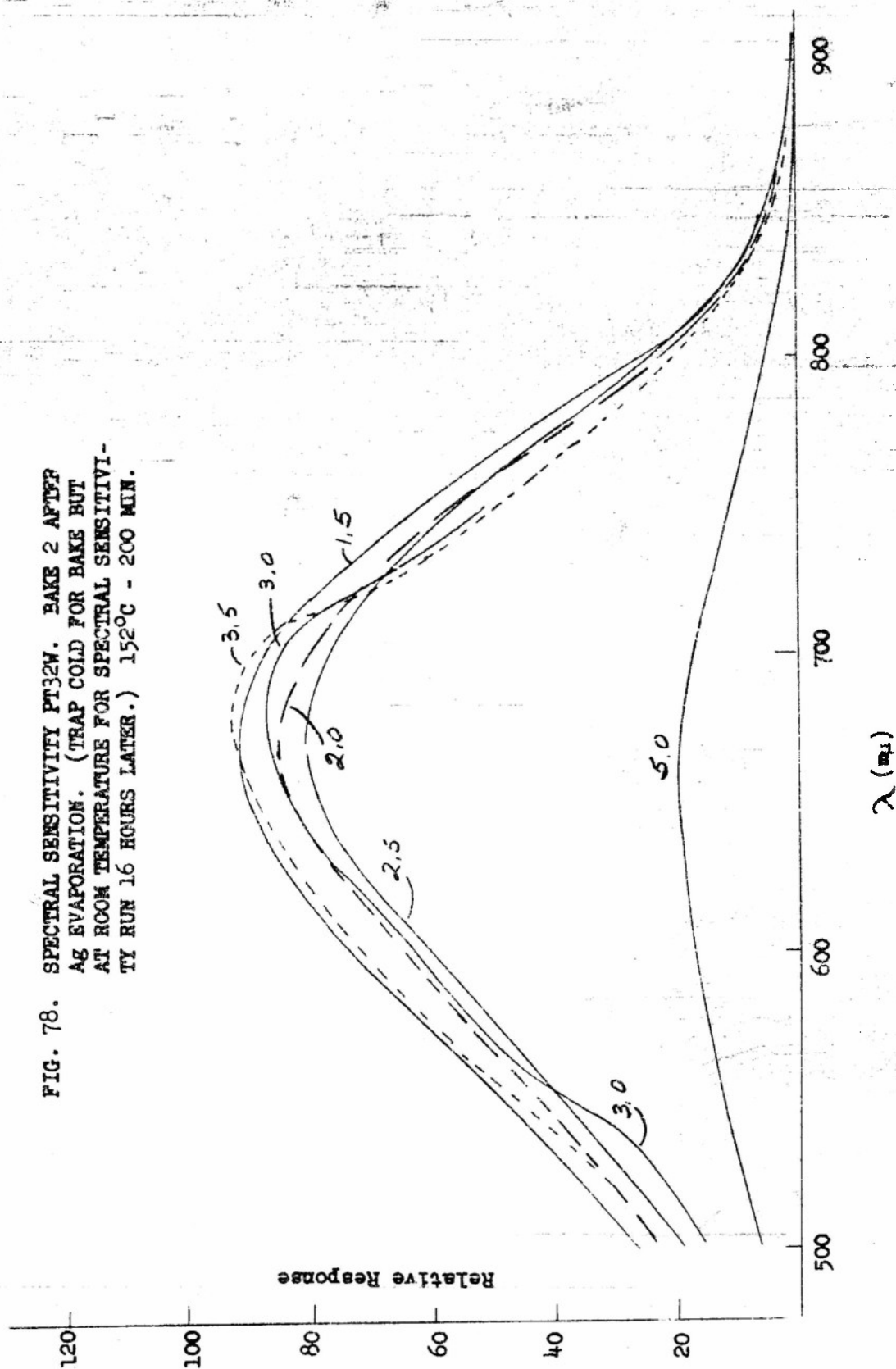




FIG. 78. SPECTRAL SENSITIVITY PT32W. BAKE 2 AFTER  
 AG EVAPORATION. (TRAP COLD FOR BAKE BUT  
 AT ROOM TEMPERATURE FOR SPECTRAL SENSITIVI-  
 TY RUN 16 HOURS LATER.) 152°C - 200 MIN.



After this second bake, silver was evaporated onto the surface to give maximum photoemission. As shown in Fig. 76 this produced a decrease in the long wavelength limit but an increase in the sensitivity in the 600  $m\mu$  region. In this figure it will be noted that the response does not vary in a systematic manner with original silver thickness. After baking for 25 minutes at 125°C with the trap cold the set of response curves shown in Fig. 77 were obtained. This increase in photoemission and the ordering of the response curves is indeed amazing. Subsequently the tube was baked for 200 minutes at 152°C. However, the spectral responses were not measured until 16 hours later. During this period of time, for the tube design used, the surface would become equilibrated with excess cesium. As shown in Fig. 78 the final responses for the region 1.5 - 3.5  $\mu$  were similar. This last set of data have no real meaning due to excess cesium on the cathode a fact which was not recognized when the measurements were made.

In considering the data reported above it is to be emphasized that the response curves are not characteristic of pure cesium. When cesium is introduced into the tube, to produce a surface which has a definite excess of cesium, the maximum response occurs at approximately 550  $m\mu$  and the long wavelength limit of 675  $m\mu$ . These cathodes are further characterized by the presence of appreciable leakage current between the electrodes. For the fabrication conditions used in the preparation of these cathodes it would be reasonable to presuppose that  $Cs_2O$  and possibly some  $Cs_7O_2$  were present in the photosurface. Experiments described in the following section in connection with the x-ray study of photosurface composition indicate that a surface containing  $Cs_3O$  will exhibit a maximum near 650  $m\mu$  and a long wavelength limit of the order of 850  $m\mu$ .

The data on the effect of the silver evaporation illustrate the marked effects which may be produced by further silver addition to a semitransparent photosurface. Such phenomena, as discussed in Section 1, have been extensively studied by Asao<sup>23</sup>.

These experiments indicated, more than anything else, the importance of further study of the baking process and especially the importance of controlling the quantity of cesium added to the cathode. The experiments were performed before the study outlined in Section 3.1 had been made, so we were not by any means certain, at the time, that extended baking would remove excess cesium from the surface.

Attention was therefore turned again to the study of the baking operation and to the study of emission during cesium addition. Further work on silver film thickness was done only much later in the cesium tracer study with the results outlined in the previous section. By the time this work had indicated the decisive importance of silver base it was too late to resume the investigation.

In conclusion, there is one further comment to be made on the validity of the idea that we can reduce the effect of uncontrolled process variables by using films of graded thickness, thus permitting the study of the effect of thickness by making measurements at different positions on the same cathode. This idea contains the implication that similar trends will be found even though integral and infrared sensitivities may vary from tube to tube. Inspection of Figs. 75, 76, and 77 shows at once that this view is fallacious. It is also evident that the character of a photocathode can be completely altered by changing a processing step. In Section 1 it was pointed out on several occasions that description of the method of cathode preparation is essential in order to properly evaluate the generality of any specific investigation of cathode properties. This could hardly be better illustrated than by the results of Figs. 75, 76, and 77. It is also evident from these figures that the effect of a baking operation performed on a semitransparent cathode can hardly be due merely to the removal of excess cesium from a photocathode although this factor is no doubt important. The diffusion and grain growth of silver are undoubtedly important in this case. This is in contrast to the case of massive cathodes prepared on a silver sheet base.

From the results of this and the previous section it is clear that much remains to be done in studying the effect of silver base on the photocathode. This is, in our opinion, the most promising direction for future investigation.

### 3.6 Photocathode Stability

In the literature relating to the Ag-O-Cs cathode references<sup>48, 49, 22</sup> appear relating to "fatigue" and "slumpage" of the photosurface. The former term is applied to change in photo response of the cathode on illumination with or without applied voltage. The latter term is generally applied to changes occurring in the surface as a function of time. Though neither phenomenon has been investigated in detail by us, some scattered data relating to these phenomena have been obtained coincident with other

studies.

Nothing of general interest relating to fatigue has been obtained in our work. The light intensities used were apparently not high enough to induce any noticeable fatigue in the majority of our cathodes. In one case a noticeable fatigue was obtained with a massive cathode and the phenomenon was studied briefly. On rebaking the tube, however, the effect disappeared so the results have no general interest and will be omitted. Reference must be made to the above work for an account of this phenomenon.

The only case of "slumpage" encountered was with a tube, PT3, prepared during the early stages of the investigation. Obviously no conclusions of practical value can be reached on the basis of the behavior of one tube. The behavior of the tube is nevertheless of some interest so the facts will be described. The results described in previous sections show clearly that a possible cause of "slumpage" is the distillation of cesium onto the photocathode at room temperature. This factor is also discussed in connection with the description of PT3. Photocathode PT3 was a good infrared-sensitive semitransparent cathode which was prepared during the early stages of the project. After the "stabilizing" bake at 130°C (Aug 15, 1950) the photosurface was characterized by a selective maximum at 920  $m\mu$  and a long wavelength limit of 1150  $m\mu$ . The spectral response determined 44 days later (Sept 28, 1950) had a maximum at 940  $m\mu$  and a long wavelength limit of 1300  $m\mu$ . When the spectral response was remeasured on Nov 19, 1951 it was found that the tube had "slumped". However, the spectral distribution maximum was at 920  $m\mu$  with the long wavelength limit at 1275 - 1300  $m\mu$ . The tube was then baked at 130°C for 30 minutes and the infrared response was recovered, the maximum being at 925  $m\mu$  and the long wavelength limit at 1350  $m\mu$ . The spectral responses before and after bake are shown in Fig. 79. In Fig. 80 the ratio of the slumped photocurrent to the stabilized tube emission is plotted as a function of wavelength. The data in this latter figure indicate that beyond 800  $m\mu$  the two responses differ primarily by a constant factor, the slumped tube current being 11% of the "stabilized" emission. This behavior agrees well with the assumption that a layer excess cesium on the cathode is the reason for the change in sensitivity on standing. On baking the cathode this layer is removed.

In the case of the massive cathode tubes which have been prepared, only minor changes in response with time are

FIG. 79. SPECTRAL SENSITIVITY PT-3.  
 A. 1.05 Yrs. AFTER LAST TEST<sup>4</sup>  
 B. After 30 Min. Bake 130°C.

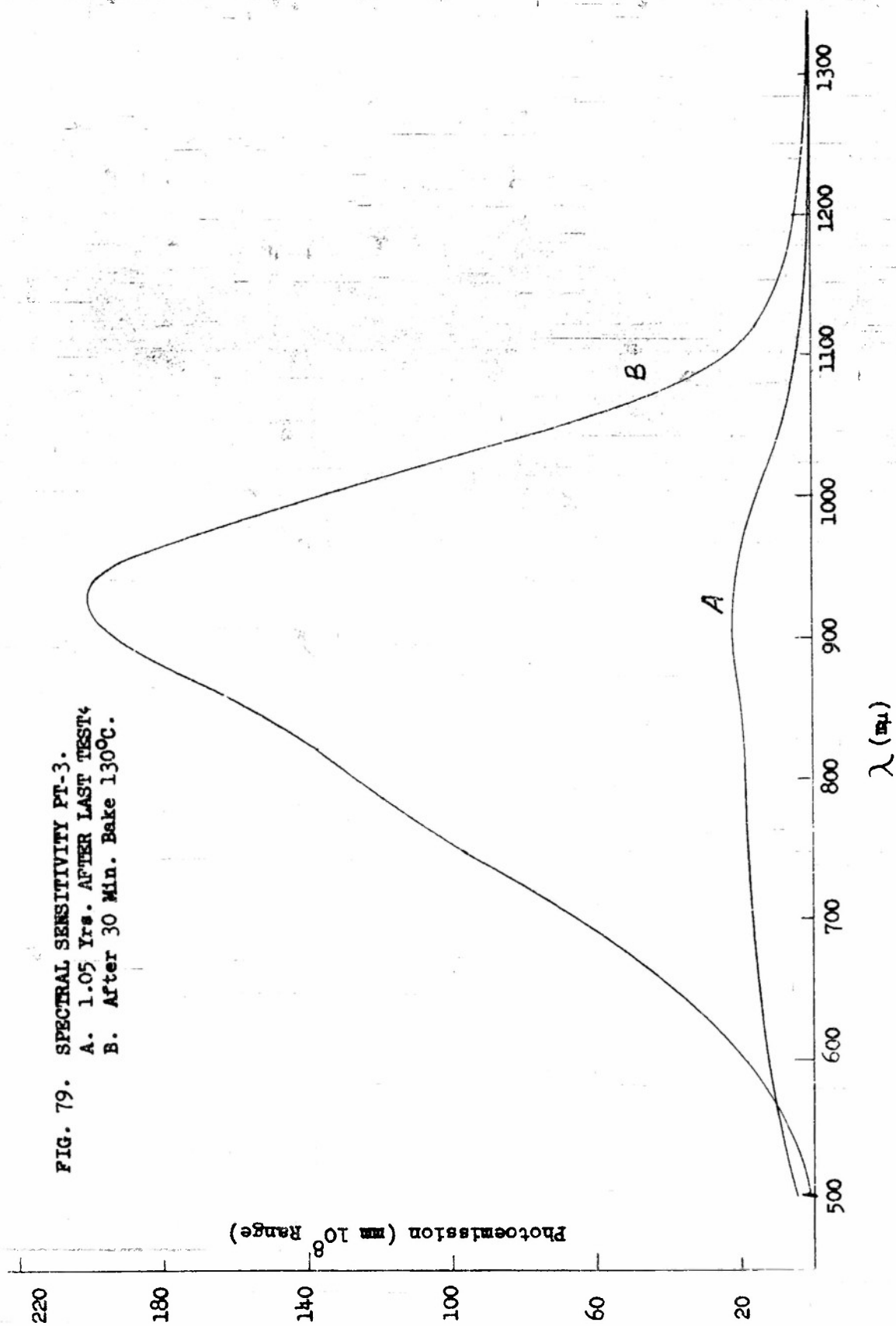
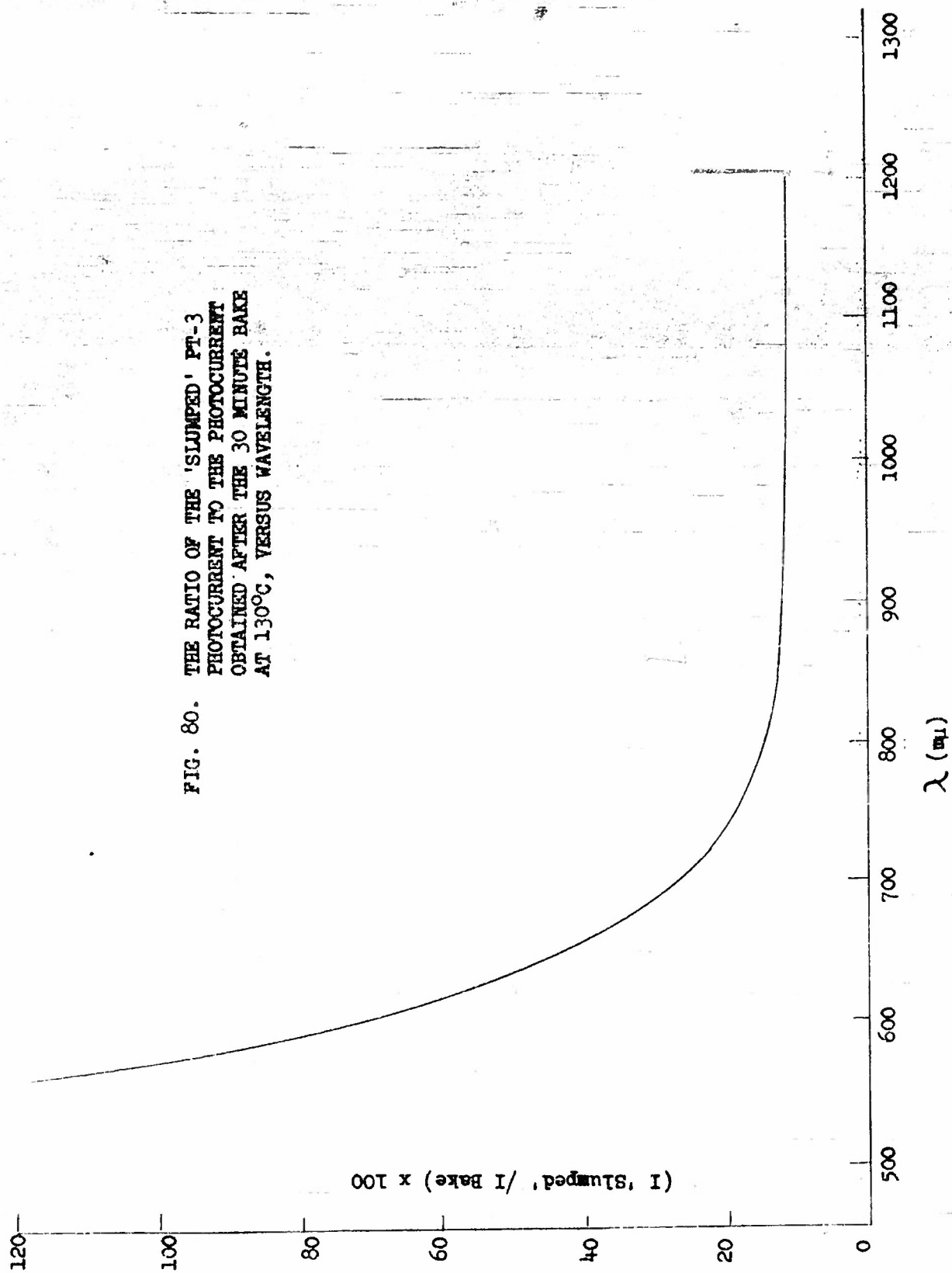


FIG. 80. THE RATIO OF THE 'SLUMPED' PT-3  
PHOTOCURRENT TO THE PHOTOCURRENT  
OBTAINED AFTER THE 30 MINUTE BAKE  
AT 130°C, VERSUS WAVELENGTH.





observed provided equilibrium has been established. For example, the massive cathode PT18 which was fabricated on November 17, 1950, had a good infrared sensitivity characterized by an emission peak at 980  $\mu$  and a long wavelength limit of 1670  $\mu$ . The spectral response was remeasured on November 19, 1951 and it was found that the maximum had shifted to 960  $\mu$  with the long  $\lambda$  limit at 1750  $\mu$  (0.708 ev.). After a half hour bake the peak shifted to 975  $\mu$  but the long wavelength limit remained at 1750  $\mu$ . The changes in the photocurrent as a function of wavelength actually were very small (<1%).

### 3.7 Summary

From the experimental results thus far described it is evident that the compound  $\text{Cs}_2\text{O}$  is, in some manner, essential to the development of infrared sensitivity in the silver-oxygen-cesium photocathode. This substance does not constitute, however, the only essential ingredient. This is indicated by the work of Section 3.51 in which a pronounced effect of silver base is demonstrated. The cathodes having low infrared sensitivity which were prepared on 10,000A silver bases (see Section 3.51) are expected to contain  $\text{Cs}_2\text{O}$  and yet the infrared sensitivity was low. Either  $\text{Cs}_2\text{O}$  did not, for some reason, form at all or, more likely, something in addition to  $\text{Cs}_2\text{O}$  is required for infrared sensitivity. The results of Sections 1.4, 1.5, 1.6 suggest that silver, finely dispersed through the  $\text{Cs}_2\text{O}$ , may be an essential ingredient. Whether this silver is dissolved in  $\text{Cs}_2\text{O}$ , forming a solid solution, or whether it constitutes a colloidal dispersion, or both, is not known. It seems, however, to be essential. According to the theory of de Boer<sup>22</sup> the function of silver is to make the  $\text{Cs}_2\text{O}$  layer conducting, while according to Sayama silver acts as the source of photoelectrons. We prefer to delay comment on this matter until Section 5. In some manner, however, the distribution of silver certainly affects infrared sensitivity.

It is also found that infrared sensitivity is greatly affected by small amounts of cesium. This effect is noticeable even at high temperatures as for example in Section 3.12 where the effect of interrupting cesium flow is discussed. If, however, a small amount of cesium is added at high temperature, e.g. 190°C, and the cesium addition is stopped then the surface quickly recovers because equilibrium is re-established and the excess cesium is used up by combination with a higher cesium oxide to form  $\text{Cs}_2\text{O}$ . At room temperature,



however, where the reaction rates are low the addition of a very small amount of cesium to an infrared-sensitive photocathode very markedly reduces the infrared sensitivity. This effect persists until the cathode is heated to re-establish equilibrium. Thus a very small amount of "adsorbed" cesium has a pronounced effect on infrared sensitivity. As explained earlier, there is no assurance that this "excess" is a stoichiometric excess beyond the composition  $\text{Cs}_2\text{O}$ . For it has not been established that the compound formed in the cathode has a composition which corresponds exactly to  $\text{Cs}_2\text{O}$ , although the results of Section 4 show that it probably does not depart far from that composition. In any case a slight change in cesium content affects infrared sensitivity and hence a cesium impurity, as well as silver, must also be considered as a factor.

Considerable evidence has been obtained that two types of emitting centers are contributing to "normal", i.e. highly infrared-sensitive, massive cathodes. This is suggested by the fact that spectral response curves which have maxima at 900  $\text{m}\mu$  or higher also have inflections (and sometimes maxima) at 750  $\text{m}\mu$ . It seems possible that the emitting centers which produce the response with a maximum at 750  $\text{m}\mu$  are involved in the photocathodes listed in Table IV of Section 1.9. It is notable that almost all of the cathodes which are specular reflectors have spectral responses at 750  $\text{m}\mu$  or at shorter wavelengths. The highly infrared-sensitive cathodes with maxima at 900  $\text{m}\mu$  or above are invariably non-specular. This is clearly demonstrated by the work of Kluge<sup>26</sup>. This strongly suggests that the work on optical properties of cathodes which are specular reflectors (see Section 1) serves to characterize only one type of emitting center, namely that which gives rise to a spectral response near 750  $\text{m}\mu$ . The other type of emitting center being produced only in non-specular reflectors has not been studied by such methods. Further discussion is postponed until the cathode composition has been discussed.

#### 4. PHOTOCATHODE COMPOSITION

- 4.1 Photosurface Composition
  - 4.11 General Problems
  - 4.12 Tube Fabrication at 190°C
  - 4.13 Tube Fabrication at 150°C
  - 4.14 Interpretation of Tracer Composition Data
- 4.2 Cathode Phase Identification
  - 4.21 Maximum Thermionic Emission 190°C Cathodes
  - 4.22 Cesium Deficient 150°C Cathodes
  - 4.23 Excess Cesium 150°C Cathodes
- 4.3 Chemical Composition and Spectral Response

#### 4. PHOTOSURFACE COMPOSITION

From the discussion given in Section 3 it is evident that determination of the total cesium entering a photocell does not constitute a satisfactory method of determining the amount on the cathode. This is demonstrated by the fact that the (Cs/O) ratio (for the photocell) at which maximum thermionic emission is obtained depends on the geometrical arrangement of the photocell elements. In order, therefore, to obtain a more direct measure of cesium on the cathode itself a radioactive cesium tracer has been used as described in Section 4.1 below.

The determination of the amounts of cesium and oxygen on the cathode does not, in itself, determine what molecular species are present unless the cathode is at equilibrium. Although, as pointed out in Section 3.1, photocathodes can be prepared which seem to closely approximate to a condition of chemical equilibrium and which are highly infrared-sensitive it is not by any means established that the cathodes prepared by the normal routine methods, similar to those used in commercial practice, are in chemical equilibrium. In fact the results of Section 3.42 suggest that equilibrium is not established in such tubes. It is of some interest, therefore, to have some means by which the compounds present in a photocathode can be directly identified. This was done by means of x-ray diffraction as described in Section 4.2 below. Unfortunately, constituents present in small proportion are hard to detect by x-ray diffraction and hence it has not proved possible to identify every phase. The dominant phases are, however, established.

Section 4.3 below contains a classification of the types of spectral responses encountered in photocathode preparation and a discussion of their relation to the chemical composition of the cathode.

##### 4.1 Photosurface Composition

The determination of the photosurface composition by the use of radioactive cesium was complicated in a number of ways. To obtain definite results considerable preliminary work had to be done. Though the experimental techniques have been discussed in Section 2 it is desirable first to briefly review the problems encountered in order to clearly indicate the experimental basis for the photosurface composition determination.

#### 4.11 General problems

One of the first problems encountered was the development of a suitable tube design. The cathode surface area had to be accurately defined so that reliable measurements of the  $^{55}\text{Cs}^{134}$  concentration could be performed. Since the pressure change during glow discharge oxidation was used to calculate the photosurface (Cs/O) mole ratio it was also necessary to utilize materials of construction which did not oxidize to an appreciable extent under the glow discharge conditions used. After considerable work the tube design discussed in Section 2.4 (see Fig. 14) was evolved. The cathode in this tube consists of a thick silver film (area  $2.86 \text{ cm}^2$ ) evaporated onto a microscope cover glass. The cathode cover glass was backed with a second cover glass to prevent the deposition of radioactive cesium on the back surface of the photocathode. Since, under the experiment conditions used, tantalum was not appreciably oxidized by the glow discharge, this substance was used to fabricate the metal components of the tube.

After the development of a suitable tube design it was necessary to develop fabrication techniques which would reduce possible sputtering of silver during the glow discharge oxidation of the cathode. This problem was solved finally by constructing an auxiliary vacuum system in which the surface could be repeatedly oxidized and decomposed to obtain a surface with satisfactory oxidation characteristics before the cathode was mounted in a tube envelope on another vacuum system.

To establish the reliability of the oxygen pressure change for the computation of the (Cs/O) mole ratio the thermal decomposition of the silver oxide produced in a glow discharge had to be investigated. It was found that on heating the oxidized cathode tube to  $190^\circ\text{C}$  there was an initial rapid evolution of a small amount of oxygen followed by a very slow decomposition of the oxide. The initial gas evolution was interpreted as originating from the adsorption of a small amount of oxygen on the tube walls during oxidation. The slow rate of oxide decomposition was considered negligible for two reasons. First, the amount of oxygen evolved during the time required to prepare a cathode would be small compared to the amount deposited. Second, under the experimental fabrication conditions the cesium addition is started during the period of heating the cathode to  $190^\circ\text{C}$ . After the addition of a small quantity of cesium it seems likely that a protective

film of cesium is formed which reduces the rate of decomposition of silver oxide. On the basis of the data on oxide decomposition at 190°C (see Part I of this Final Report Series) it was concluded that at 150°C the rate would be vanishingly small.

The determination of the cesium content of the final photocathode was performed by comparing the radioactivity of the cathode disc to that of standard discs containing a known amount of the cesium tracer mixture used to prepare the pellets. To develop the technique for preparing and measuring the activity of the discs considerable experimentation was required. The final procedure used is described in Section 2.4.

The errors involved in the determination of the cathode composition are discussed at the end of Section 2.4. The maximum error in the calculated cathode (Cs/O) mole ratio is considered to be 15% assuming that no oxygen is lost from the cathode during tube fabrication. As stated in Section 2.4 the probable error is estimated as about one third of this value.

#### 4.12 Tube fabrication at 190°C

The cesium-oxygen phase diagram indicates that at 190°C the equilibrium phases which may form are as follows (see Section 3.1):  $O_2(s)$ - $CsO_2(s)$ ,  $CsO_2(s)$ - $Cs_2O_3(s)$ ,  $Cs_2O_3(s)$ - $Cs_2O(s)$ , and  $Cs_2O(s)$ - $Cs(l)$ . The investigation of the cesium oxides in bulk quantities suggests that in traversing the phase diagram from the oxygen rich side the  $Cs_2O_2$  phase is not readily formed. Assuming this is correct then it would be predicted that the cathode (Cs/O) mole ratio would lie in the range  $0.66 < (Cs/O) < 2.00$  if phase equilibrium is established and if  $Cs_2O$  is the electron emitting species. Furthermore, for the more sensitive surfaces it would be anticipated that the ratio would approach 2.0 as a limit. In the study of the development of photoelectric and thermionic emission at 190°C it was found that the (Cs/O) mole ratio was of the order of 1.6 - 1.8 for the more sensitive infrared cathodes.

As discussed in Section 3.51 the thick evaporated silver cathode exhibited, during the early stages of the investigation, a very erratic behavior during the cesium addition. Much experimental work at numerous compositions and under a variety of conditions was necessary in order to locate the source of trouble. In view of the variety of

conditions used and the rather surprising results finally obtained it seems desirable to describe the results as they actually developed rather than to lump together the data on all photocathodes. This procedure is followed below, a description of processing conditions and results being given for each photocathode and the reasons, which prevailed at the time of the experimentation, being given in each case.

Before proceeding to the discussion of results it is worthwhile to recall that if the cesium addition is continued for a sufficient time beyond the maximum thermionic emission there is first a large drop in the tube current, almost to zero, followed ultimately by a marked increase. This increased current, however, varies with voltage in accordance with Ohm's law and is, therefore, attributed to conduction by a surface film on the phototube envelope (see Section 3.1). An additional observation which throws some light on the nature of this film was made during this composition study and is also discussed below. The fabrication data for the 190°C tubes are summarized in Table XIV. The table headings are, for the most part, self explanatory. In the remaining cases the headings will become clear from the subsequent text.

Five non-radioactive tubes were initially prepared to develop the fabrication technique. In the preparation of PT1588-92 no cesium flow data were obtained since no restricting capillary was used. Consequently excess cesium was introduced. The first four tubes were fabricated on the vacuum system while the fifth was prepared using the oven system technique described in Section 2.12. Consequently, reliable cesium flow data were not obtained during the fabrication of the first four tubes.

During the fabrication of PT1588-93 (Tube No. 2) thermionic emission developed during cesium addition, increased rapidly to a maximum, and then decreased. The spectral response after tip off was characterized by a maximum at 690 and a long wavelength limit at  $\sim 980$  m $\mu$ . Baking the cathode at 1250°C for 1 hour shifted the maximum to a combination 750 - 900 m $\mu$  response maxima curve with a long wavelength limit at 1150 m $\mu$ . A second bake of an hour at 1300°C produced a marked 750 m $\mu$  maximum, an inflection point at 900 m $\mu$ , and a shift of the long wavelength limit to 1250 m $\mu$ . This surface probably was deficient in cesium since the cesium source was actually cooled before the maximum thermionic emission was reached.



TABLE XIV. FABRICATION DATA FOR 190°C TRACER TUBES

No.	Cathode	Date	Silver Thickness (A) $\times 10^{-3}$	Volume of System (cm <sup>3</sup> )	Oxygen Take-up (microns)	Atom Moles Oxygen $\times 10^7$	Capillary Length (cm)	Dimensions Radius (cm) $\times 10^2$
1	1588-92	2-21-52	10	325.4	11	3.82	--	--
2	1588-93	3-6-52	10	~"	20	~6.96	--	--
3	1588-94	3-19-52	10	~"	--	--	--	--
4	1588-98	3-25-52	10	~"	79	27.4	--	--
5	1588-107	4-25-52	10	~"	59	20.4	2.3	1.00
6	659-16	6-16-52	10	273.5	42	12.7	6.0	2.29
7	659-19	6-18-52	10	276.8	25	7.5	3.8	2.29
8	659-28	6-24-52	10	275.0	103	31.0	3.0	3.44
9	659-33	7-1-52	10	276.2	83	24.2	3.0	3.44
10	659-42	7-10-52	10	285.5	43	13.2	3.1	3.44
11	659-46	7-16-52	10	284.2	42	12.6	6.0	2.29
12	1588-111	7-23-52	10	274.2	37	10.6	6.0	2.29
13	1588-115	7-24-52	10	~280.0	~39	~11.5	6.0	2.29
14	1588-117	7-29-52	33	~285.0	~56	~17.1	6.0	2.29
15	1588-122	8-5-52	20	286.6	56	13.7	3.1	3.44
16	1588-130	8-13-52	47	294.7	91	28.7	3.1	3.44
17	1588-137	8-21-52	6	287.4	60	18.3	3.0	3.44
18	1588-145	8-26-52	48	284.7	54	16.3	2.9	3.44



TABLE XIV. (Continued)

No.	Oven Temp. (°C)	Cesium Flow Rate (Moles/min) $\times 10^9$	Oven Warm up Time (min)	Total Time Cesium Cooled (min)	Total Time(1) Cesium Flow (min)	Total Moles Cesium Introduced $\times 10^6$
1	--	--	--	--	--	--
2	--	--	--	--	--	--
3	--	--	--	--	--	--
4	--	--	--	--	--	--
5	150	397.0	16	--	35.0	13.9
6	189	9.35	26	2.5	1456.5	13.6
7	190	15.48	22	6.0	129.0	2.00
8	190	66.24	32	2.0	104.5	6.92
9	191	69.12	15	--	190.5	13.2
10	190	64.14	15	11.0	160.5	10.3
11	190	9.79	16	31.5	1091.5	10.7
12	190	9.79	40	--	170.0	1.66
13	190	10.19	~16	11.0	391.0	3.99
14	190	10.19	~16	2.0	319.0	3.25
15	184	49.90	24	8.5	76.5	3.82
16	189	61.26	20	15.0	117.5	7.20
17	190	66.24	22	19.5	71.5	4.74
18	190	68.52	20	2.0	188.0	12.9

(1) Subtracting one half the time for oven warm up and total time cesium was cooled.

TABLE XIV. (Continued)

No.	Pressure at seal-off (2) (mm) $\times 10^6$	(Cs/O) flow	Moles Cesium counted on cathode $\times 10^6$	(Cs/O) count	Spectral Data (millimicrons) (3)		
					Peak	Height	Long
1	x scale	--	--	--	620	760	950
2	2.8	--	--	--	750/900	980	1250
3	--	--	--	--	--	--	--
4	3.5	--	--	--	955	1070	1400
5	~6.0	6.81	--	--	765	880	1100
6	21.0	10.71	--	--	~500	--	~900
7	7.0	2.65	0.35	0.28	500	--	860
8	6.9	2.23	3.12	1.01	920	1010	1350
9	10.0	5.45	5.07	2.10	--	--	--
10	4.9	7.80	1.04	0.79	615	715	850
11	10.0	8.49	0.72	0.57	630	735	950
12	6.9	1.57	0.85	0.80	370	--	--
13	5.6	~3.47	--	--	635	740	1000
14	10.0	~1.90	--	--	950	1075	1350
15	5.6	2.79	2.04	1.49	950	1080	1350
16	6.3	2.51	2.30	0.80	920	1020	1250
17	5.6	2.59	2.26	1.23	935	1035	1250
18	6.9	7.91	0.92	0.57	--	--	--

(2) As read on a VG 1 A ion gauge tube.

(3) For surface immediately before counting in the case of radioactive tubes. Other tubes are listed as best infrared surface attained. Position is approximately center of cathode surface.

TABLE XIV. (Continued)

No.	T.E.	Even Data (mm on 105)				(L)	F <sub>2</sub> /F <sub>1</sub>	F <sub>5</sub> /F <sub>1</sub>	Peak Height of Spectral Response Curve. (3) (mm on 108)
		F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	F <sub>4</sub>				
1	---	---	---	---	---	---	---	---	8.2
2	98.0	---	---	---	---	---	---	---	57.0
3	31.5	---	---	---	---	---	---	---	---
4	208.0	---	---	---	---	---	---	---	176.0
5	12.5	---	---	---	---	---	---	---	95.0
6	2.15	380.0	5.0	---	---	---	0.0131	0	---
7	1.38	72.0	0.3	---	---	---	0.00417	0	---
8	73.0	450.0	245.0	115.0	80.0	40.0	0.545	0.0890	92.0
9	39.0	250.0	77.0	26.0	19.0	12.0	0.308	0.0480	---
10	1.1	290.0	4.0	---	---	---	0.0138	0	17.5
11	10.4	144.0	21.0	8.0	6.0	2.0	0.146	0.00139	46.0
12	0.72	21.0	~0.02	---	---	---	~0.000953	0	---
13	13.2	230.0	48.0	16.0	12.0	5.0	0.208	0.0218	26.5
14	---	---	---	---	---	---	---	---	145.0
15	152.0	450.0	220.0	120.0	89.0	45.0	0.489	0.1	176.0
16	59.0	74.0	19.5	7.5	4.5	2.5	0.264	0.0338	44.0
17	66.0	180.0	68.0	30.0	21.0	11.0	0.378	0.0611	59.0
18	210.0	~80.0	37.0	15.0	10.0	5.0	~0.462	~0.0625	---

(L) Values given are maximum whether cesium addition stopped or not.

TABLE XIV. (Continued)

No.	Spectral Response (3) at 900 millimicrons (mm on 108)	Mole % (5) Cs <sub>2</sub> O	Cs Flow (6) (monolayers per minute)	Cs on (7) Back Disc (moles/cm <sup>2</sup> ) (monolayers) x 10 <sup>9</sup>	Cs on Back Disc	Ratio Cs on Cathode to Disc
1	0.3	--	--	--	--	--
2	54.0	--	--	--	--	--
3	--	--	--	--	--	--
4	152.0	--	--	--	--	--
5	32.0	--	228.0	--	--	--
6	--	none	5.36	29.87	48.6	3.11
7	0	15.0	8.86	9.89	16.1	14.92
8	91.0	51.0	38.0	20.79	33.8	39.50
9	--	102.0	39.6	22.85	37.2	58.40
10	0	23.0	36.8	48.51	78.9	5.64
11	0	none	5.61	22.04	35.8	8.54
12	0	25.0	5.61	9.02	14.7	28.18
13	0	--	5.84	--	--	--
14	237.0	--	5.84	--	--	--
15	163.0	83.0	28.6	10.22	16.6	52.52
16	43.0	25.0	35.2	26.69	43.4	22.68
17	57.0	69.0	38.0	11.75	19.1	50.62
18	--	none	39.2	34.80	56.6	6.99

(5) Assuming all cathode is a mixture of Cs<sub>2</sub>O and Cs<sub>2</sub>O<sub>3</sub>.

(6) Assuming one cesium atom occupies an area of 2.7x10<sup>-15</sup> cm<sup>2</sup>.

(7) The cathode area is 2.86 cm<sup>2</sup>. The tube envelope area is approximately 80 cm<sup>2</sup>.

Tube 1588-94 (No. 3) exhibited an abnormal behavior during cesium addition. The cathode did not have appreciable infrared sensitivity after fabrication and on cooling the cesium source the current rose slightly and then decreased immediately. The voltage dependence of the tube current was not studied in detail and therefore it is not possible to propose an explanation for the observed behavior.

The following tube, 1588-98, was the first successful tube made. This tube developed more thermionic emission than the other three and the emission doubled on cooling the cesium source. After tip off the spectral response was characterized by a flat maximum extending from 750 to 910  $\mu$  and a long wavelength limit of 1200  $\mu$ . After a series of 5 bakes at 130°C, 160°C, and 180°C a final response was obtained characterized by a 955  $\mu$  maximum and a 1400  $\mu$  long wavelength limit. On baking the surface for 153 minutes at 190°C the spectral response finally changed to a low integral response having a 650  $\mu$  maximum and a 1000  $\mu$  long wavelength limit. This tube has been discussed in detail in Section 3.42.

The remaining tubes were fabricated using a fine capillary to limit, and measure, the cesium flow rate. The technique of Section 2.12 was used. The next tube, 1588-107, was made at 150°C. Because of an error in the cesium flow calculations excess cesium was introduced into this tube. After fabrication the response could not be readily measured because of the excess cesium introduced. After a 70 minute bake at 180°C with the cesium source cooled in a dry ice-acetone mixture a photosurface was obtained which exhibited a 765 maximum and a 1250  $\mu$  long  $\lambda$  limit. Excess cesium still remained in the tube.

At this point the method of following photosensitivity using light filters (see Section 2.12) was introduced. Furthermore radioactive cesium was used for the remaining tubes with the exception of 1588-115 and 1588-117.

The first tracer tube, 659-16, did not develop appreciable thermionic emission and the emission dropped on cooling the cesium source. Furthermore, only  $F_1$  response was developed to an appreciable extent and decreased markedly on cooling the cesium source. This behavior is, of course, quite abnormal. The tube was left in the oven overnight and in the morning was in the conduction region. The cathode count gave a 0.28 (Cs/O) ratio which could not be understood since the ratio computed from the flow rate through the capillary was 10.71. It is to be noted that the flow rate

in this case, and in all subsequent cases in the present section, was computed from the intermediate pressure flow equation.

Tube 659-19 was fabricated in a manner similar to 659-16 but the cesium addition was discontinued before the conduction region was reached. This tube did not develop appreciable thermionic emission and the current also decreased on cooling the cesium source. This is again abnormal. After fabrication, the spectral response maximum was near 500  $m\mu$  with a long wavelength limit of approximately 900  $m\mu$ . After baking for 40 minutes at 130°C the maximum shifted to less than 500  $m\mu$  and the long wavelength limit to 850  $m\mu$  while the photocurrent decreased by a factor of approximately two at all wavelengths. The (Cs/O) ratio by count was higher this time, 0.74, and the (Cs/O) by flow was lower than the previous tube; namely, 2.65. This information seemed conflicting, the more cesium introduced the less the amount on the cathode.

The fabrication procedures were carefully considered at this point and everything seemed in order; however, the lack of thermionic emission could not be explained. It was noticed that the silver oxide coat had a rather shiny unoxidized appearance so in the next tube the silver was first oxidized and then decomposed in order to better prepare the base surface for oxidation. In addition,  $31.0 \times 10^{-7}$  gramatoms of oxygen was deposited in the next tube as compared to  $7.54 \times 10^{-7}$  in tube 659-19.

The following tube, 659-29, showed that the modification of the procedures apparently improved the emission of the surface. On cooling the cesium source beyond the composition 2.2 (Cs/O) the emission increased. (In these tubes the cathode area relative to the tube wall area was small so that appreciably more cesium was required to react with the glass surface than for the tubes of Section 3.1. Consequently the (Cs/O) ratio by flow measured not only the cesium reacting at the photosurface but also included a considerable fraction contributed by wall reaction.) The final photosurface exhibited a response similar to commercial massive cathode surfaces; namely, a maximum at 920  $m\mu$ , a half maximum photocurrent wavelength of 1010  $m\mu$ , and a long  $\lambda$  limit of 1350  $m\mu$ . The (Cs/O) ratio for the photosurface determined from the cathode activity was 1.01 while the ratio determined from the rate of flow through the capillary was 2.23. Thus the ratio obtained by counting increased again and the flow value decreased.

It had been observed that a rather large  $F_1$  response developed during the early stages of fabrication. Since the



initial oxidation step required a higher voltage discharge than after the surface had been oxidized and decomposed it was thought that possibly sputtered silver (or silver oxide) on the wall might be contributing to the odd behavior of the (Cs/O) ratios. Consequently in subsequent tubes the silver films were initially oxidized in an auxiliary vacuum system. The oxide was then decomposed by heating the disc prior to mounting in the tube envelope. This oxidation-thermal-decomposition cycle was repeated several times if necessary to insure uniform oxidation.

Tube 659-33 was prepared in this manner and the cesium addition was continued until the conduction region was reached. This was done in order to obtain a complete emission curve to see the maxima developed and to again check the confusing result of the (Cs/O) mole ratio for the cathode decreasing with increasing amount of cesium added. As shown in Figs. 81 and 82 the behavior during cesium addition was normal. The numbers along the curve of Fig. 81, and in subsequent similar figures, give the cesium to oxygen ratio at various stages as calculated from the rate of cesium flow through the capillary. This time the (Cs/O) ratio by count was 2.10 while the flow value was 5.45.

In the following tube, 659-42, the oxygen deposited was decreased by a factor of two. This tube during fabrication did not behave "normally". Thermionic emission did not develop and cooling the cesium source caused the observed current to decrease before the conduction region was reached. The final surface was characterized by a maximum at 615  $m\mu$  and a long wavelength limit of 850  $m\mu$ , a typical excess cesium surface. This tube had a (Cs/O) ratio by count of 0.79 and by flow a ratio of 7.80. It was now concluded that the (Cs/O) by count versus (Cs/O) by flow must have a maximum.

To determine the influence of the cesium addition rate, the rate for 659-46 was decreased by a factor of 8; namely, from  $64.14 \times 10^{-9}$  to  $9.79 \times 10^{-9}$  moles of cesium per minute. During fabrication the emission characteristics were the same as for the previous tube but more  $F_2$  response was developed. The final response had a peak at 630  $m\mu$  and a long  $\lambda$  limit of 950  $m\mu$ . The cathode had a ratio of 0.57 (Cs/O) by count and 8.49 by flow.

On reconsidering the data it was observed that in the previous tubes which developed thermionic emission the initial oxide decomposition had been performed in the tube envelope whereas in the poor tubes the oxide decomposition had been performed by heating in air. The possibility was considered that the difficulties in tube preparation were due to contamination during the oxide decomposition in air, consequently the auxiliary vacuum system was modified so that the



FIG. 81. THERMIONIC EMISSION DATA.  
TRACER TUBE 659-33.

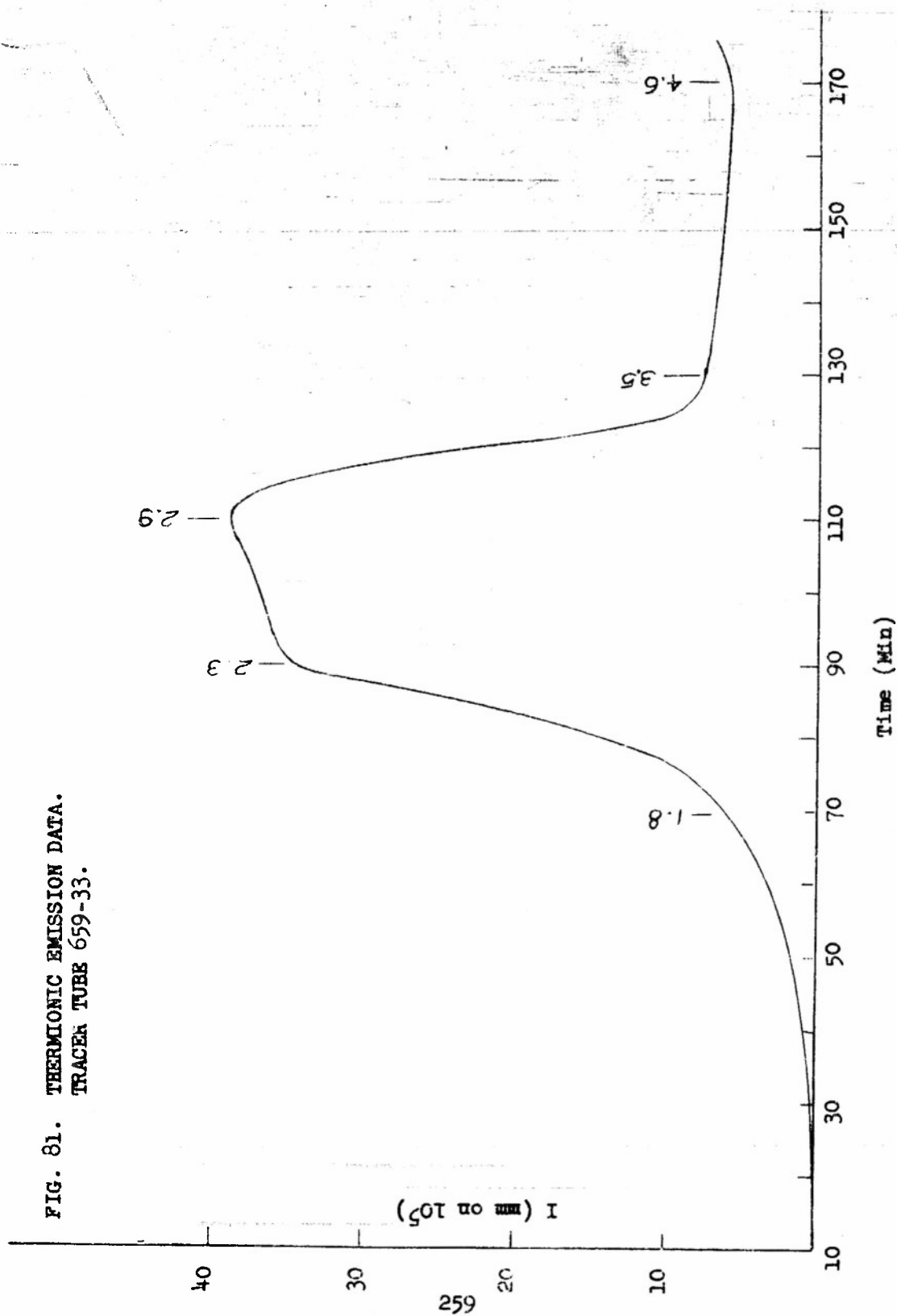
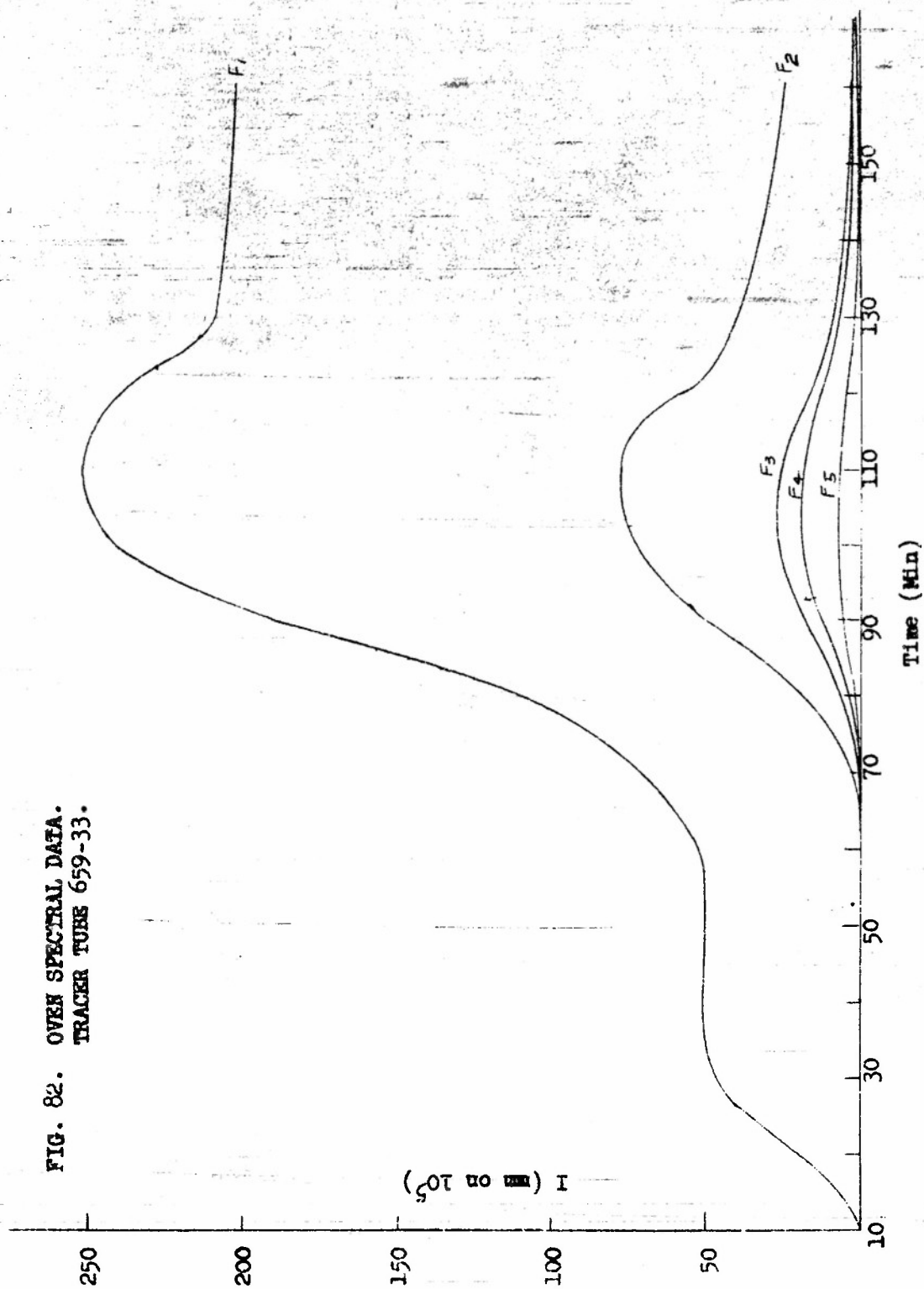


FIG. 82. OVEN SPECTRAL DATA.  
TRACER TUBE 659-33.



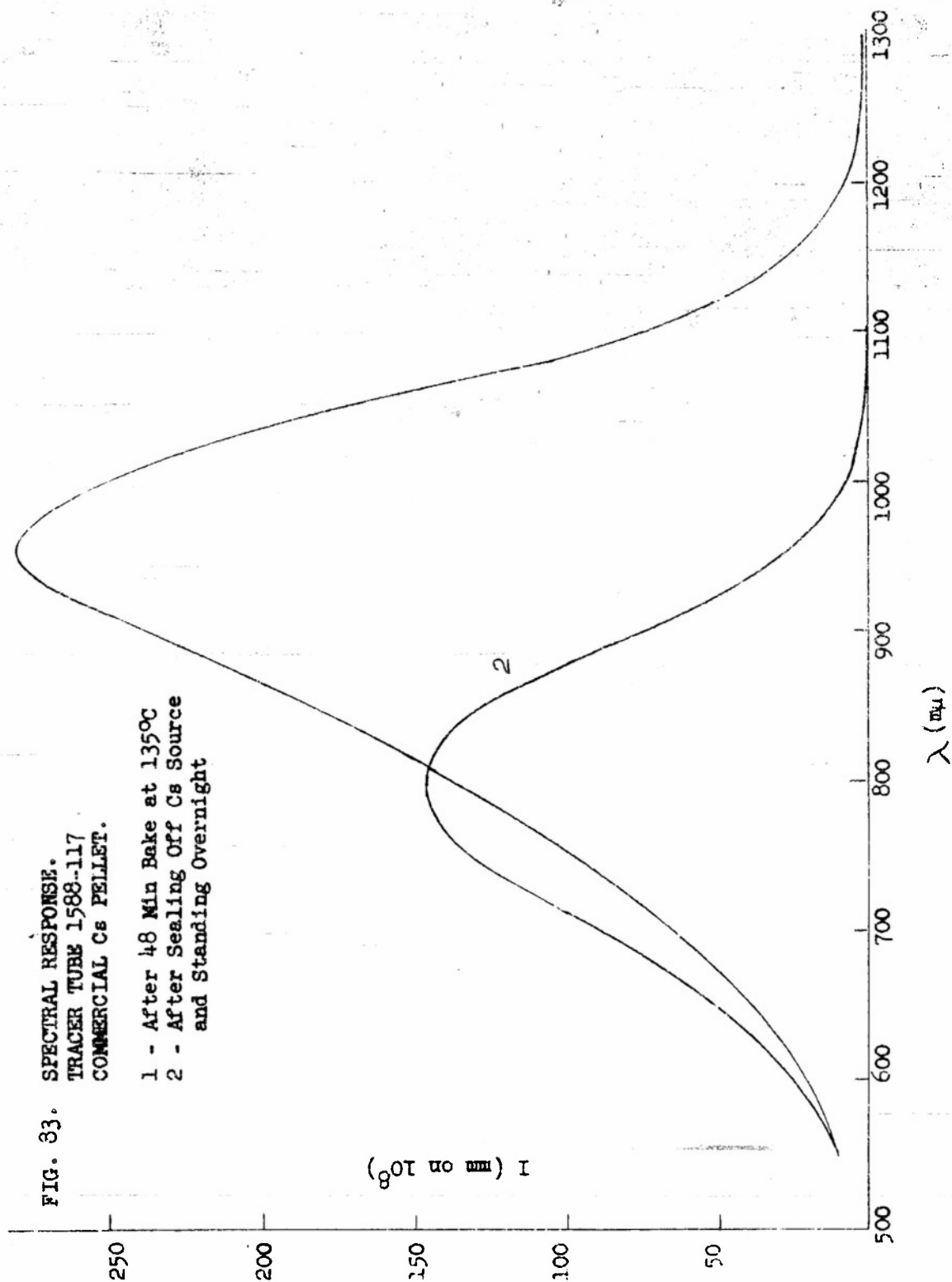
cathode surface could be oxidized and then decomposed by heat treatment in a vacuum.

This technique was used in fabrication of tube 1588-111 but it did not change the emission characteristics during fabrication. The spectral response was practically flat from 370 to 425  $m\mu$  with a slight peak at 370  $m\mu$ . This cathode had a (Cs/O) ratio by count of 0.80 and by flow of only 1.57. It is possible that during the fabrication of this tube insufficient cesium was added. The behavior was so abnormal that it could not be decided when the flow should be stopped.

Now since 1588-98 was a good non-radioactive tube and seven poor radioactive cesium tubes had been prepared, it was decided to again try a commercial  $\text{Si-Cs}_2\text{CrO}_4$  pellet to see if the difficulties encountered were associated with the cesium pellet preparation. Tube 1588-115, prepared with a commercial pellet, exhibited the same behavior as the previous poor tubes. The current during cesium addition was primarily conduction in character, and appreciable thermionic emission was not developed. The final (Cs/O) ratio by flow was 3.47, the spectral response maximum was at 635  $m\mu$  and the long wavelength limit at 1000  $m\mu$ .

The data at this point were carefully examined and it was concluded that the trouble was related to the silver base, perhaps through the oxidation step. To more nearly approach the massive cathode tube characteristics it was decided to increase the silver film base thickness above 10,000A. This effect was tested with a non-radioactive tube 1588-117 which had about three times more silver evaporated on the glass disc than in the previous tubes, 33,000A compared to 10,000A. Unfortunately during the fabrication the recorder was not used so that complete thermionic emission and spectral data were not obtained. However, as shown in Fig. 83, this tube had a normal spectral response, the maximum being at 950  $m\mu$  and the long wavelength limit at 1350  $m\mu$ . On sealing off the cesium source the response maximum shifted to 790  $m\mu$  and the long  $\lambda$  limit to 1100  $m\mu$  due to the introduction of a small amount of excess cesium (see Section 3.41). Thus increasing the silver thickness resulted in a good tube.

In the following tube the cesium flow rate was increased to  $49.9 \times 10^{-9}$  moles/minute from the value of approximately  $10 \times 10^{-9}$  used in the previous four tubes. The silver thickness in this case was 20,000A compared to 10,000A in the earlier tubes. The tube behaved normally during the fabrication in the oven. Appreciable thermionic emission developed and increased markedly on cooling the cesium source. The cesium



addition was continued until the thermionic emission maximum was passed as shown in Fig. 84. The corresponding oven spectral data are shown in Fig. 85. The development of  $F_1$  response at a very early stage (see Fig. 85) was shown in later experiments to be associated with the deposition of a cesium layer on the tantalum clips supporting the cathode. This tube gave a cathode (Cs/O) ratio by count of a 1.49 and a (Cs/O) ratio by flow of 2.79. The spectral response curves before cesium source seal off, after seal off, and after an equilibrating bake are shown in Fig. 86.

Using a similar fabrication procedure, tube 1588-130 was prepared using a 47,000A thick silver film. This tube, as did all subsequent tubes with a thick silver film, behaved "normally" throughout the processing. The cesium addition was discontinued slightly beyond the thermionic emission maximum. The final spectral response, after cesium seal off and an equilibrating bake of 94 minutes at 150°C, had a maximum at 920 and a long wavelength limit of 1250  $m\mu$ . The cathode count gave 0.80 (Cs/O) while the flow ratio was 2.51.

To obtain further data on the effect of the silver film structure on the emission characteristics, the tube 1588-137 was prepared. In this case a 6000A silver film was deposited using an evaporation rate of approximately 600A / hour compared to the 10,000A in 15 minutes used in the previous tubes. This resulted in a silver film with a very aggregated structure. This surface during fabrication behaved normally. The final cathode was semitransparent and exhibited a maximum at 935  $m\mu$  and a long wavelength limit of 1250  $m\mu$ . This tube has been discussed in Section 3.51. The count on the cathode gave a (Cs/O) ratio of 1.23 while the flow data gave a ratio of 2.59.

The data accumulated thus far defined a definite maximum in the (Cs/O) ratio by count versus (Cs/O) by flow curve as shown in Fig. 87. The points corresponding to (Cs/O) by flow greater than 6.0 had, however, been tubes which did not behave normally during the fabrication. Consequently tube 1588-145 was made in which the cesium source was cooled at the thermionic emission maximum to establish whether normal behavior was obtained. That such is the case is indicated in Figs. 88 and 89. Cesium addition was then continued to give a final (Cs/O) ratio of 7.91 by flow. The final cathode count gave (Cs/O)=0.51 and the data fitted the curve defined by the tubes considered as a whole.

FIG. 84. THERMIONIC EMISSION.  
TRACER TUBE 1588-122.

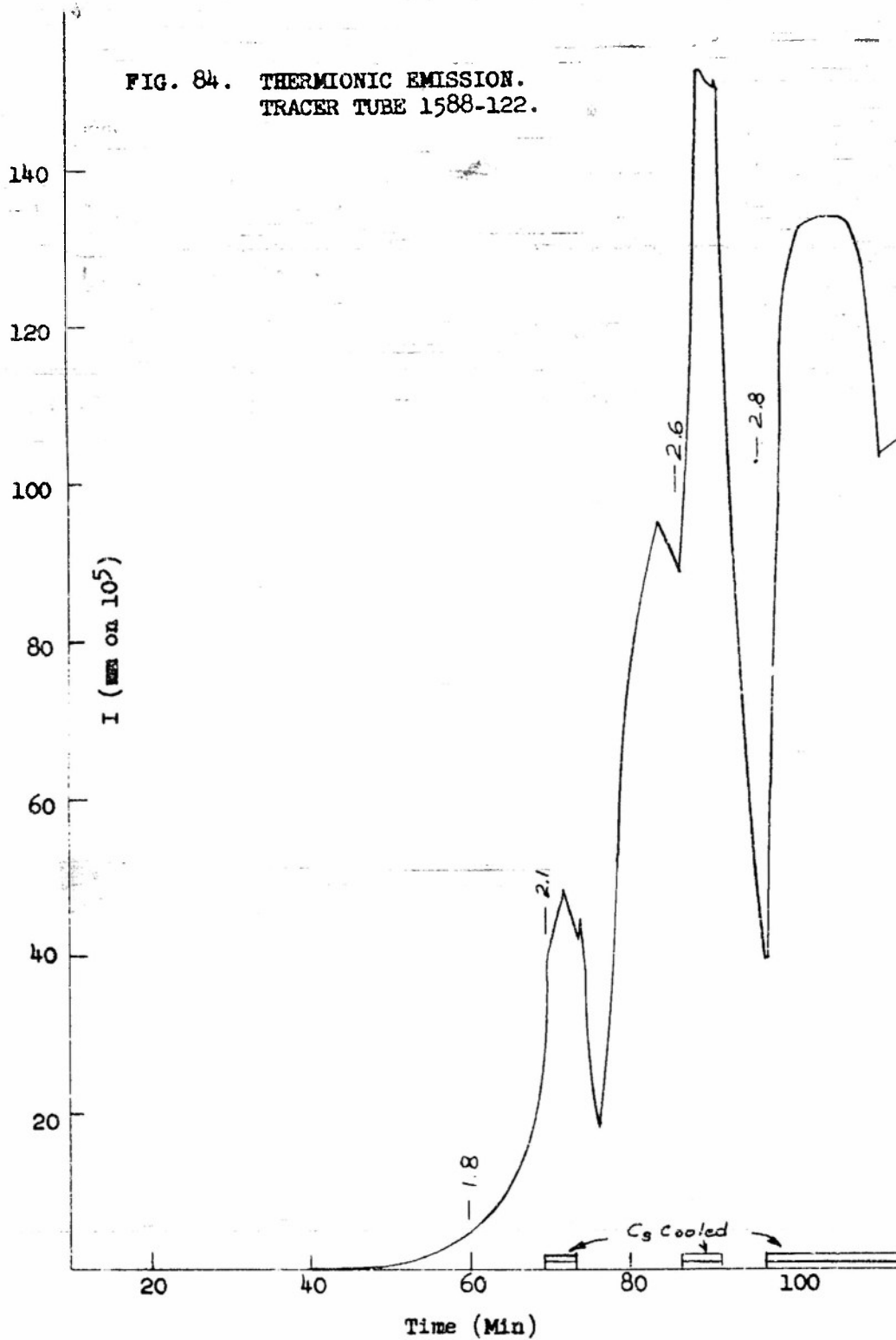


FIG. 85. OVEN SPECTRAL DATA.  
TRACER TUBE 1588-122.

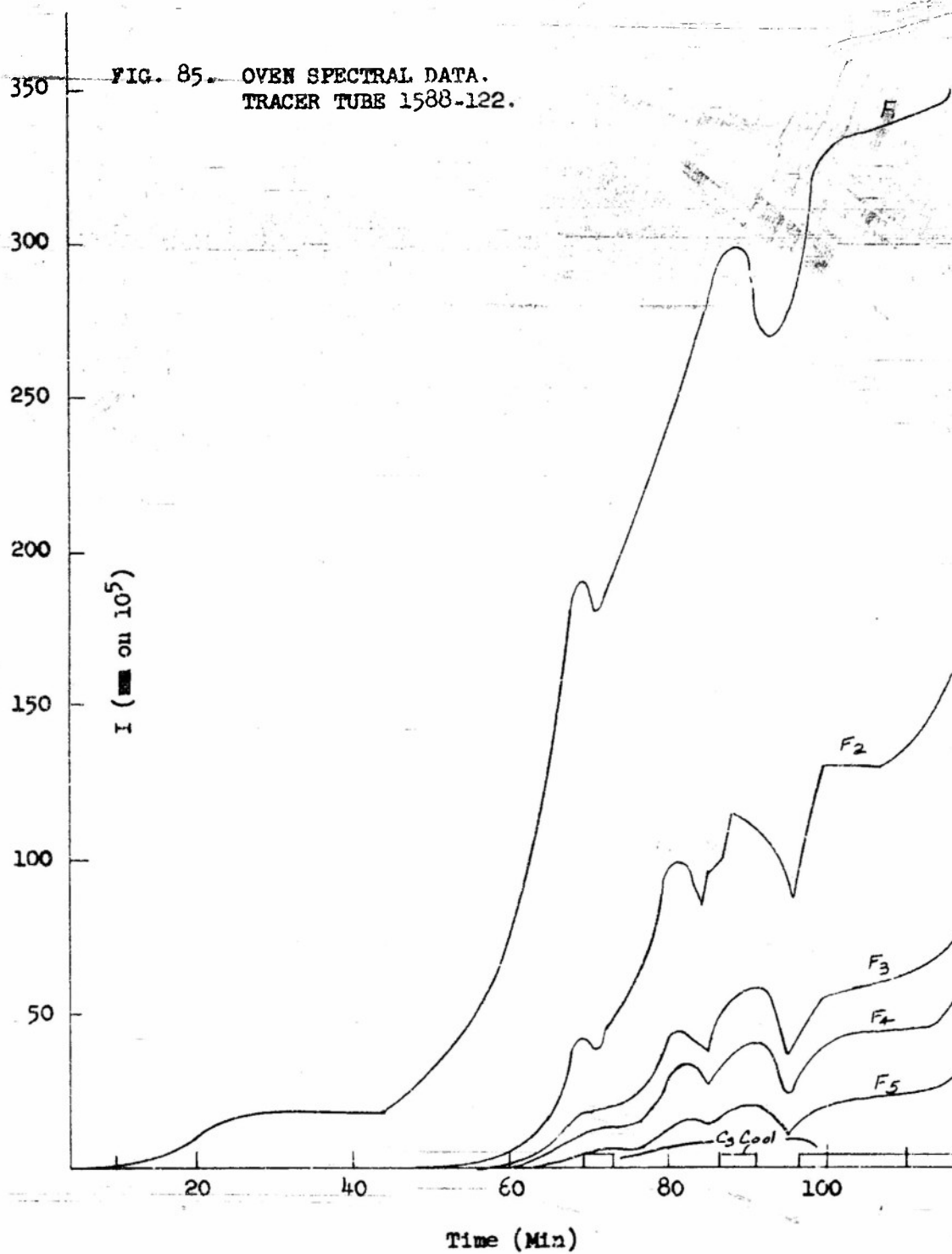
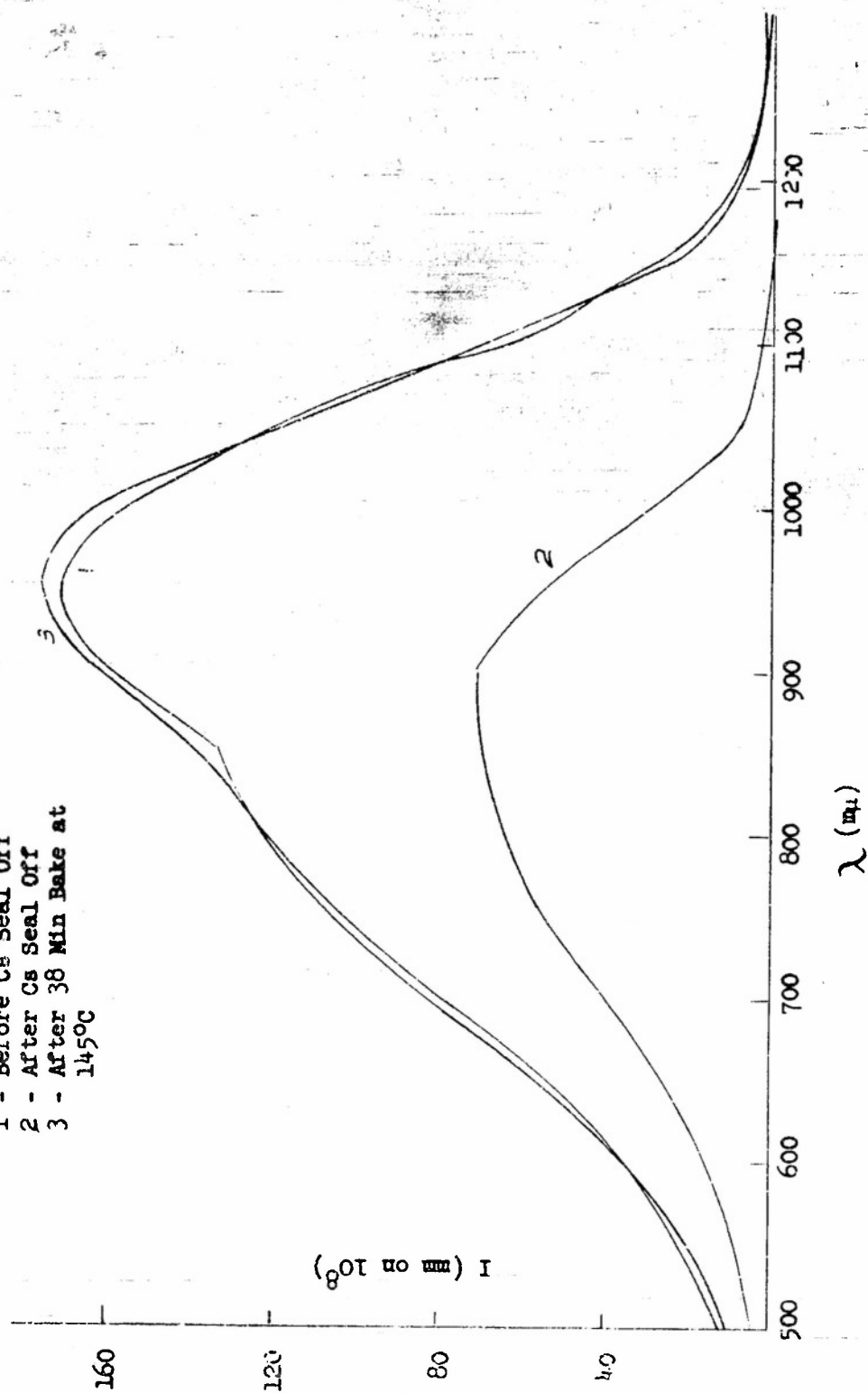
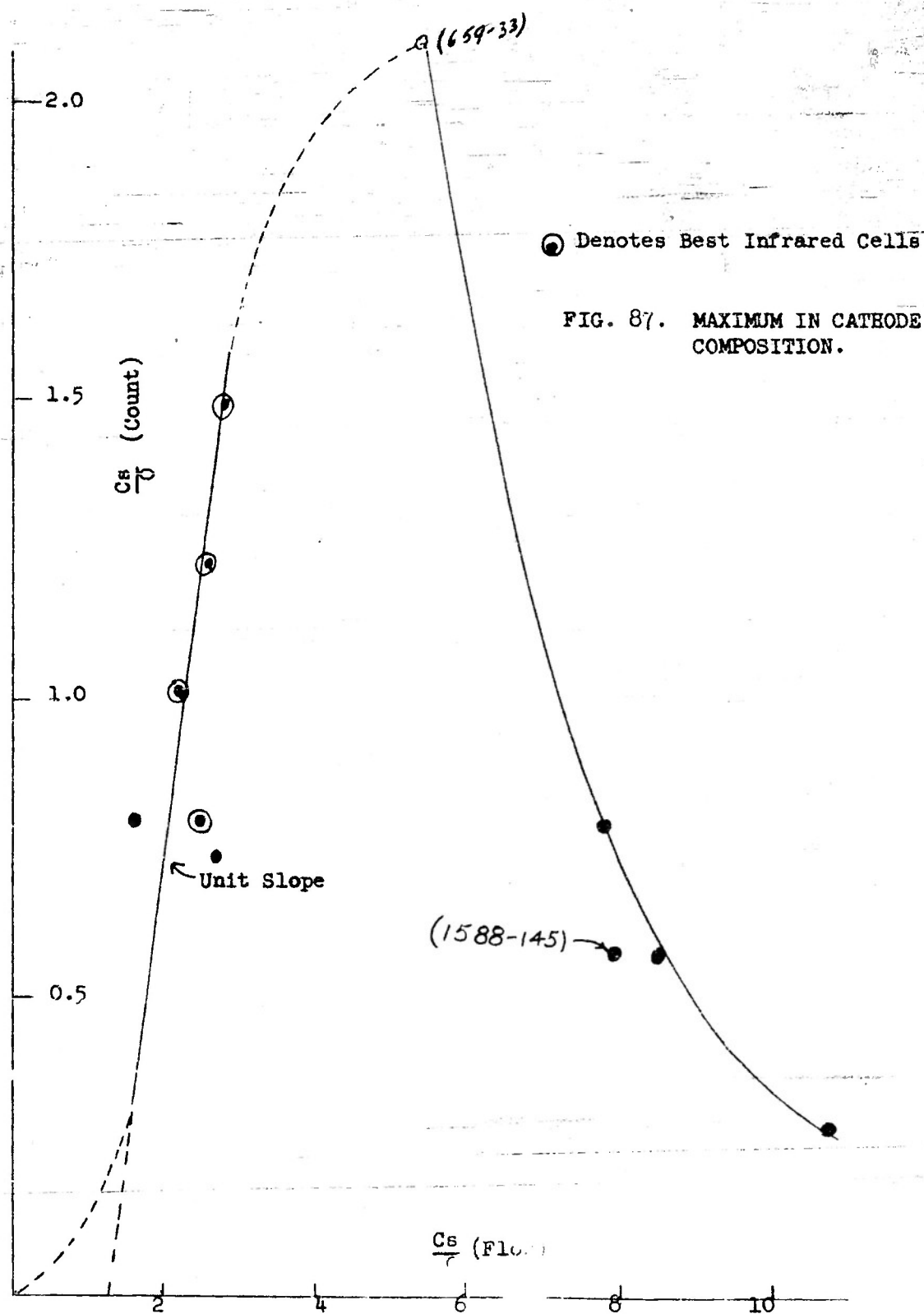




FIG. 86. SPECTRAL RESPONSE.  
TRACER TUBE 1588-122.

- 1 - Before Cs Seal Off
- 2 - After Cs Seal Off
- 3 - After 38 Min Bake at 145°C





The thermionic and photoelectric emission characteristics of this tube (1588-145) during fabrication are shown in Figs. 88 and 89 respectively. During the cesium addition into the conduction region an interesting observation was made. As shown in Fig. 90 the conduction current initially increased rather slowly and then finally increased rapidly. On cooling to room temperature the spectral response characteristics could not be determined because of the large leakage current. In the case of tubes in which sufficient cesium is added to establish a small conduction current the film exhibits a positive temperature coefficient of conduction characteristic of a semiconducting surface. With sufficient excess cesium, cooling the tube does not eliminate the leakage current. However, the resistance increases with time at room temperature due to the accumulation of the cesium on the photosurface.

A possible interpretation of the abrupt change in slope in Fig. 90 is that the initial conduction film corresponds to the formation of a semiconducting surface cesium oxide ( $\text{Cs}_x\text{O}_y$ ) film. This surface with the addition of sufficient cesium is changed to a metallic conductor corresponding to a large cesium excess. An alternative interpretation is that the film during the early stages corresponds to discrete islands of excess cesium on cesium oxide which on cooling the tube aggregate and this produces a positive temperature coefficient of conduction, the rapid increase with sufficient cesium then corresponding to the formation of a continuous film. On the basis of the available data a choice between these hypotheses is not possible.

Before proceeding to the description of the tubes prepared at  $1500^\circ\text{C}$  it is of interest to consider the possibility of thermal decomposition of silver oxide at  $190^\circ\text{C}$  before reaction with cesium takes place. The thermal decomposition of thick oxidized silver films has been studied at  $190^\circ\text{C}$ . The data are given in Fig. 8, Curve C, of Part I of this Final Report Series. From this figure it is evident that on heating the tube containing oxidized silver a very rapid initial increase in pressure takes place and thereafter the pressure increases very slowly with increasing time. The question arises as to whether this initial pressure increase is due to decomposition of oxide on the cathode or to desorption of oxygen from the glass wall of the tube envelope. The amount of oxygen evolved is equivalent to about 0.3 monolayer of  $\text{O}_2$  distributed over the tube envelope and hence it seems quite possible that desorption is involved. If this is correct then the oxygen involved is not included in

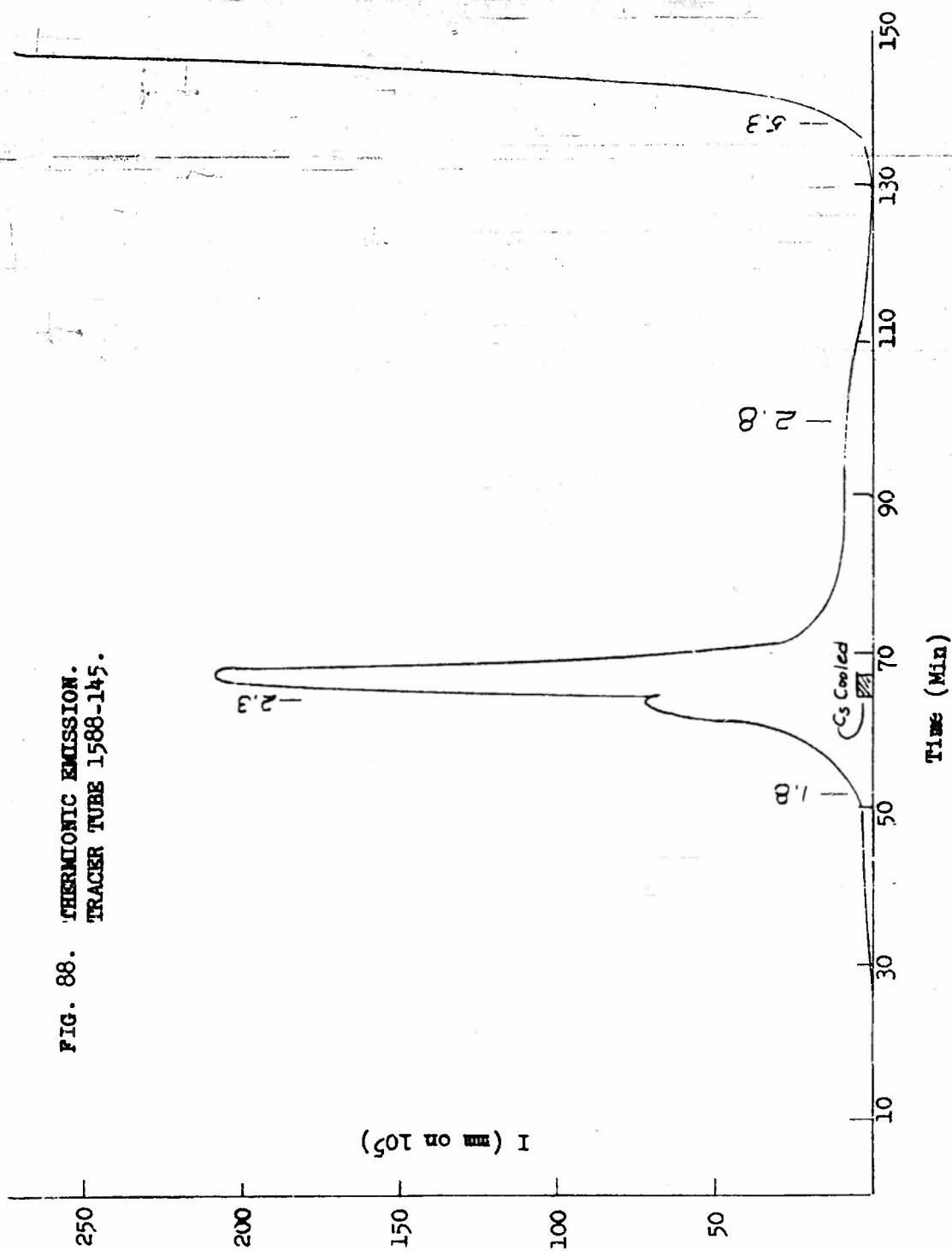
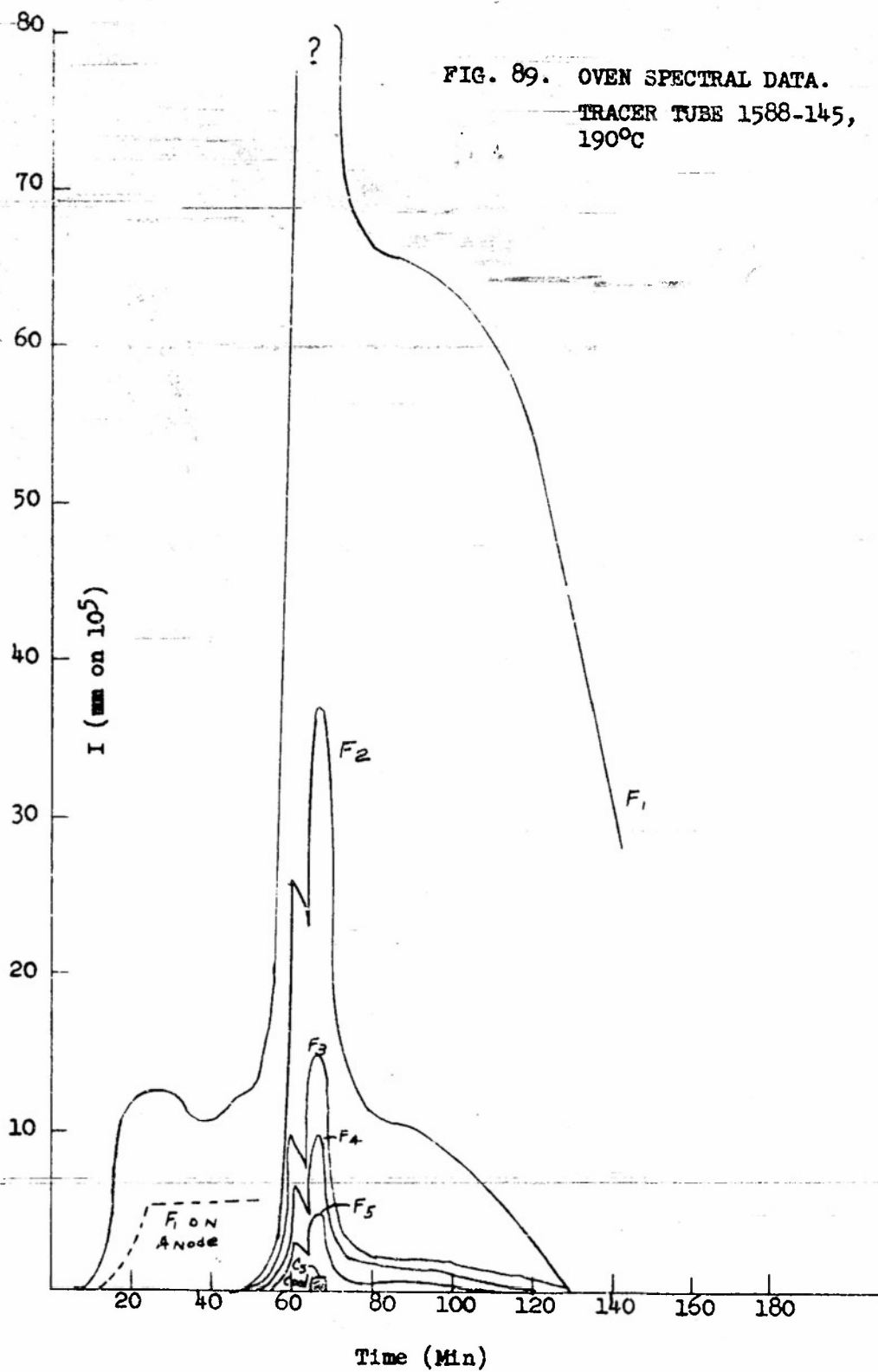


FIG. 88. THERMIONIC EMISSION.  
TRACER TUBE 1588-145.



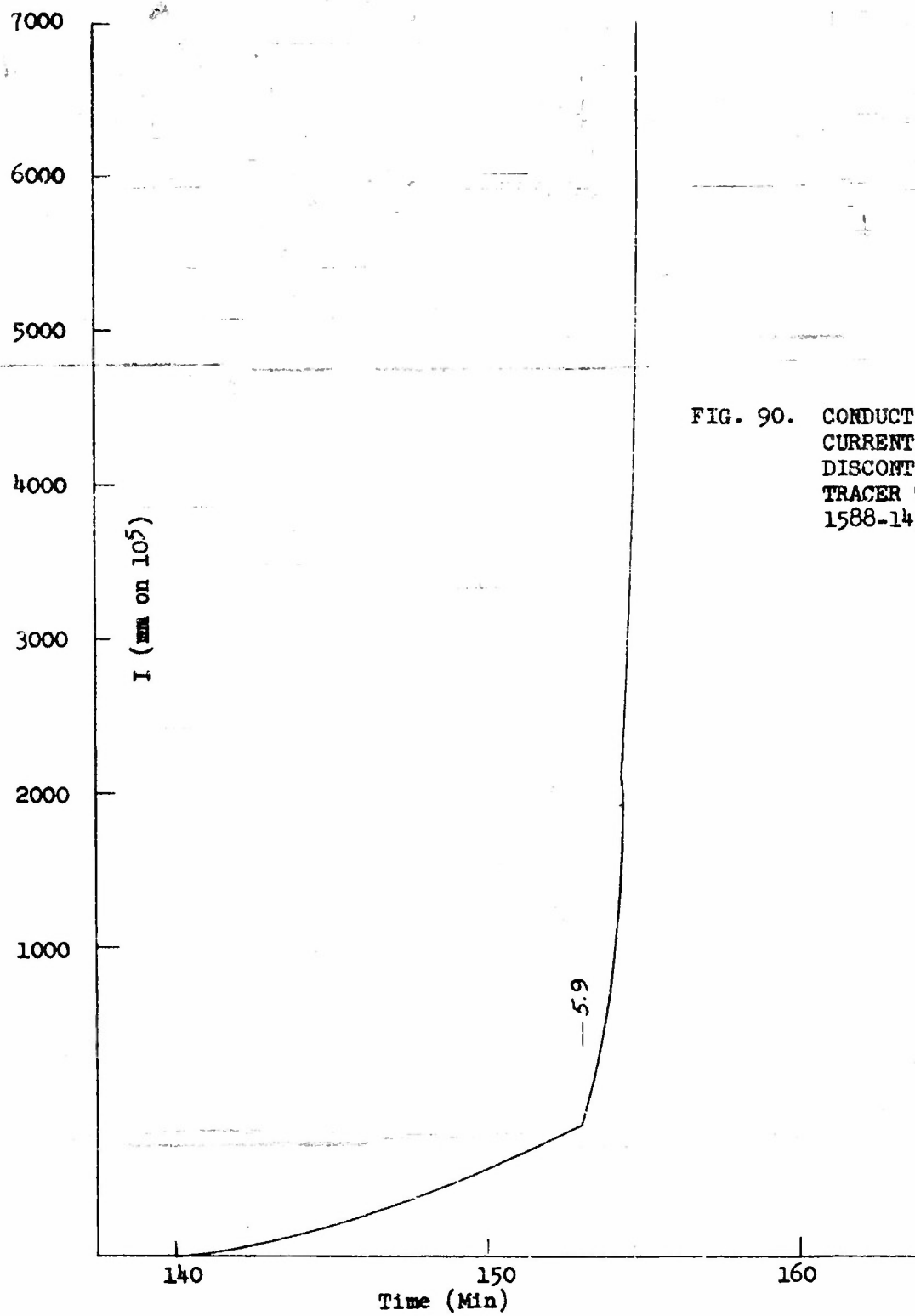


FIG. 90. CONDUCTION  
CURRENT  
DISCONTINUITY -  
TRACER TUBE  
1588-145.

that calculated from the pressure decrease on glow discharge oxidation because the same amount of oxygen is adsorbed both before and after the glow discharge oxidation. The pressure decrease during oxidation would then measure the amount of oxygen on the cathode. Oxygen desorbed from the tube walls is, of course, present to react with cesium entering the tube but the bulk of the reaction product no doubt collects on the walls of the tube envelope rather than on the cathode. No correction is required, therefore, in order to obtain the (Cs/O) ratio for the cathode. For this reason no correction has been made in the (Cs/O) ratios.

#### 4.13 Tube fabrication at 150°C

During tube fabrication at 190°C as described in the preceding section it was not possible to obtain a good infrared-sensitive photosurface which had a cathode (Cs/O) ratio of greater than 1.5. Now at 150°C the additional phase equilibria,  $\text{Cs}_2\text{O(s)}-\text{Cs}_2\text{O(s)}$ ,  $\text{Cs(l)}-\text{Cs}_2\text{O(s)}$  may be established during the tube fabrication. It was consequently of interest to determine whether or not the (Cs/O) count versus (Cs/O) flow curve had a maximum for tubes fabricated at 150°C and whether a good cathode could be obtained having a (Cs/O) ratio significantly greater than 2.0. Due to limitations of time less data could be collected at 150°C than at 190°C.

The fabrication data for the six 150°C tubes which were prepared are summarized in Table XV. The six tubes correspond to the preparation of tubes having gross compositions, calculated by the intermediate pressure region cesium flow equation, of 2.98 to 10.9. After the desired amount of cesium had been added the cesium source was cooled and the tube baked until appreciable infrared emission had been recovered. In these tubes sufficient cesium was not actually added to cause the conduction current to rise markedly. After the bake, the tube was cooled to room temperature and the spectral response determined. After the fabrication of tubes 1588-180 and 192 the cesium source was sealed off and the tube rebaked at 150°C to recover the infrared sensitivity lost by the addition of a small amount of cesium from the source. The other four tubes were counted immediately after fabrication without a preliminary sealing off of the cesium source and baking. This procedure was followed to reduce the time required to complete the processing.

In the preparation of tube 1588-180 the cesium addition was continued to a tube gross composition of 2.98. This corresponded to adding cesium beyond the thermionic emission



TABLE XV. FABRICATION DATA FOR 1500C TRACER TUBES

Tube No.	Code No.	Moles Cs on Back Disc x 10 <sup>-8</sup>	Moles Cs Cathode x 10 <sup>-6</sup>	%.atom O <sub>2</sub> on Cathode x 10 <sup>-6</sup>	(Cs/O) Count	(Cs/O) Flow	Ratio Cs Cathode to Disc	Spectral Response			
								Max. m $\mu$	Long $\lambda$ m $\mu$	Max. $\lambda$	Peak m $\mu$ (mm 10 <sup>8</sup> )
14	1588-165	1.20	7.892	3.82	2.07	3.72	650	910	1250	1030	160
15	1588-180	1.53	4.976	3.27	1.52	2.98	325	870	1300	1005	86
16	1588-186	1.99	2.927	2.076	1.41	4.95	143	875	1150	985	61
17	1588-192	1.54	1.75	0.879	1.99	7.168	114	930	1300	1050	150
18	1588-198	4.33	2.733	1.733	1.59	5.06	63	800/930	1350	1070	38
19	1588-200	3.72	1.519	1.198	1.27	10.9	41	780/875	1200	980	38

TABLE XV. (Continued)

Tube No.	Cs Flow Rate moles/min $\times 10^8$	Total Time Cs Added (min)	Cs Cool Bake Time (min)	After Cs Source Seal Off		Time TE=0 to Cs Cool (min)
				Bake Time (min)	Bake Temp. (°C)	
14	7.81	196	56	none		42
15	6.96	140	20	111	150	0
16	6.96	148	58	none		~26
17	6.96	90.5	56	70	150	~45
18	6.96	126	82	none		33
19	6.96	188	66	none		125

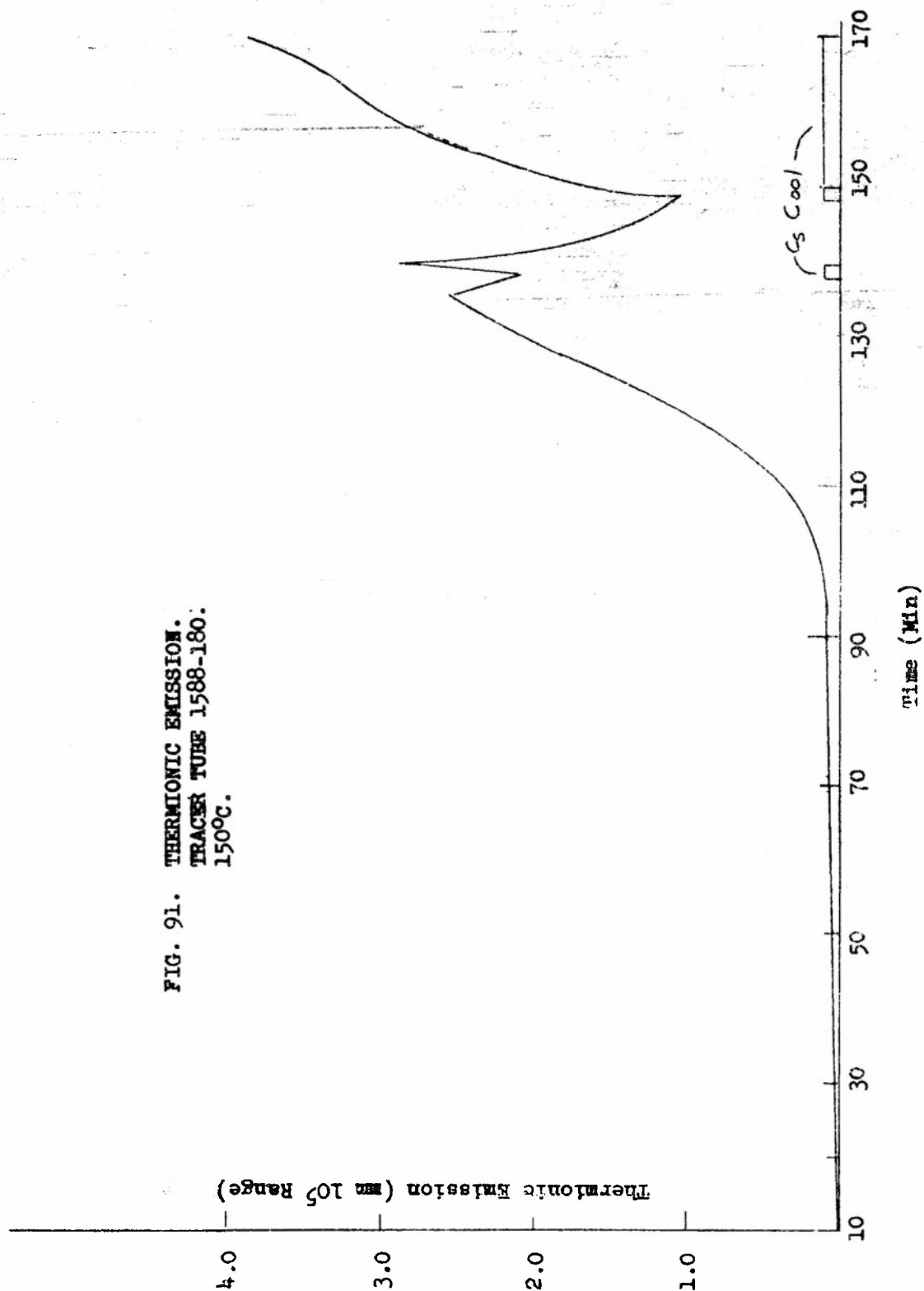
maximum as shown in Fig. 91. On cooling the cesium source there was a marked increase in the thermionic emission and a corresponding increase in the  $F_2$  response as shown in Fig. 92. After sealing the cesium source off, the spectral response curve exhibited a maximum at 650  $m\mu$  and a 950  $m\mu$  long  $\lambda$  limit. Baking at 150°C for 111 minutes resulted in a recovery of the infrared sensitivity as shown in Fig. 93. The form of the spectral response curve after bake, is typical of a surface which contains some excess cesium. With sufficient baking the infrared response would be improved and more cesium probably distilled from the cathode. This cathode was characterized by a 1.52 cathode (Cs/O) ratio determined by count compared to 2.98 by flow. These data are similar to those obtained during tube fabrication at 190°C.

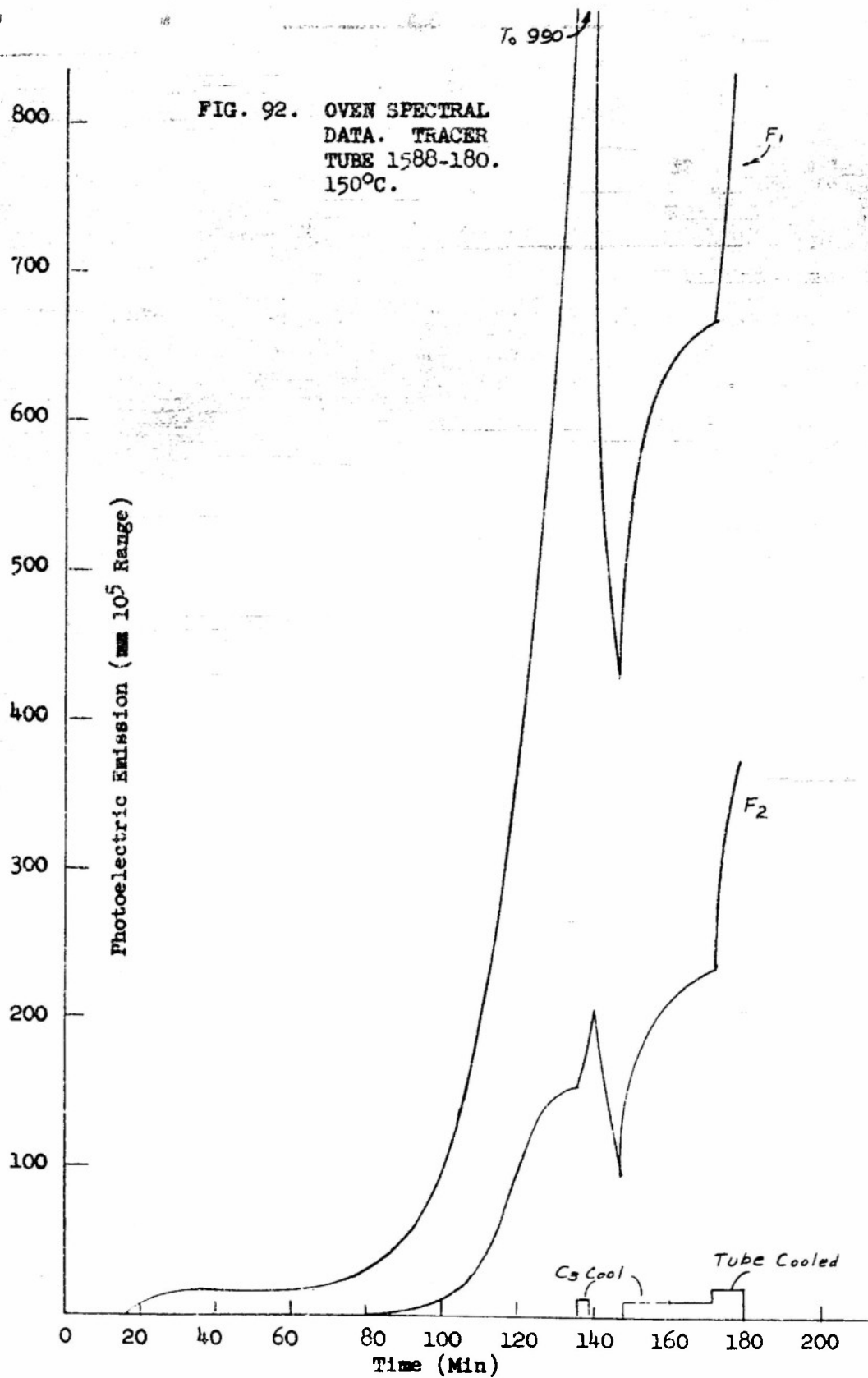
During the fabrication of the other 150°C tubes the cesium addition was continued beyond the maximum thermionic emission. Actually, before the cesium source was cooled, the thermionic emission was practically zero for the time intervals shown in the last column of Table XV. Furthermore, the  $F_2$  relative to  $F_1$  response was practically eliminated before the cesium source cool.

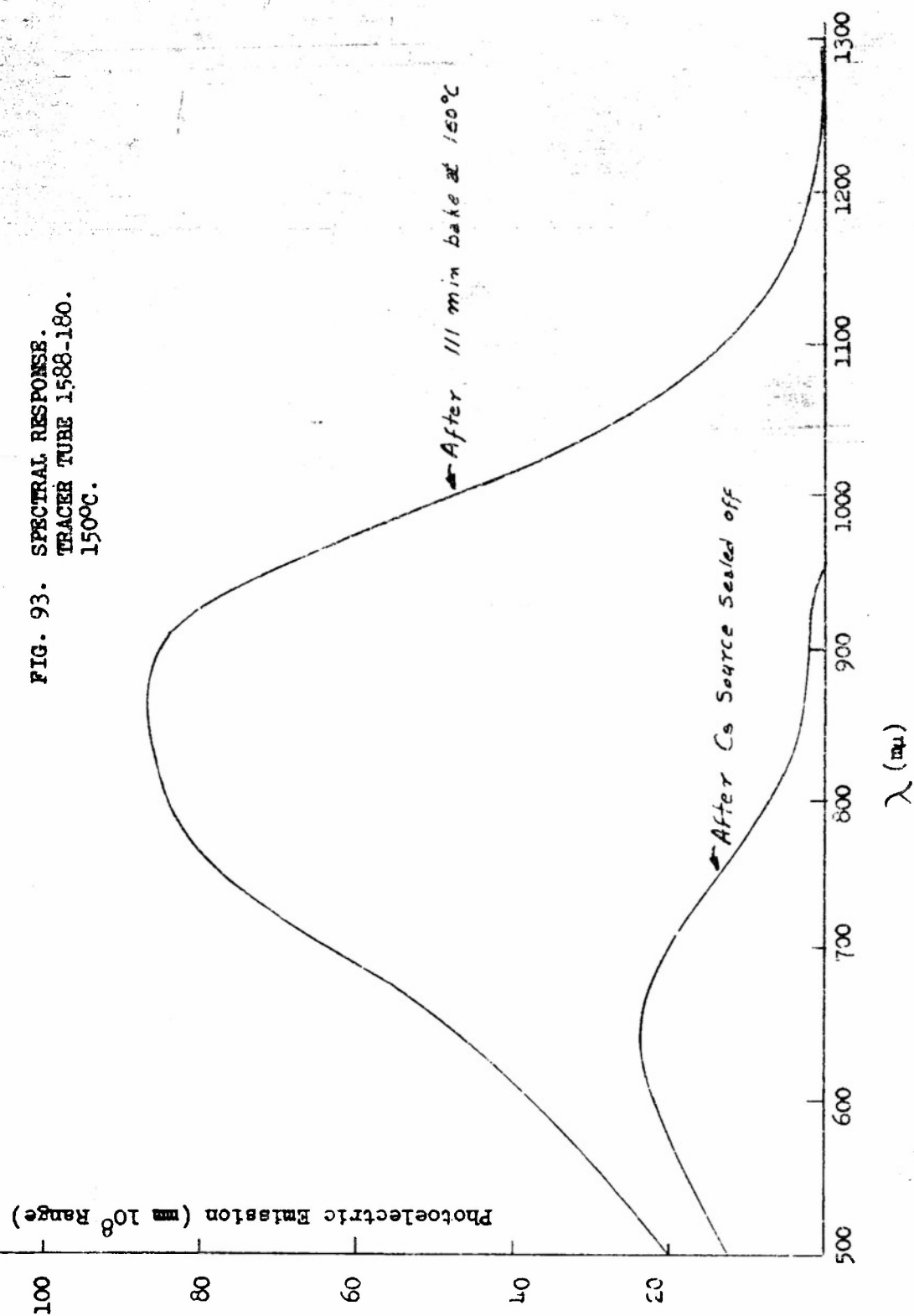
The behavior of these excess cesium cathodes is illustrated by the data obtained during the fabrication of tube 1588-198. The thermionic emission and oven spectral data for this tube are shown in Fig. 94. It is worthwhile noting that at the thermionic emission maximum the cesium source was momentarily cooled and a marked increase in thermionic emission occurred. The cathode therefore behaved "normally". As shown in Fig. 94 the thermionic emission and the infrared responses were nearly zero from 100 to 133 minutes. Cooling the cesium source at 133 minutes resulted in a gradual return of thermionic emission. Before the thermionic emission had reached a stable value the tube was cooled to room temperature and the typical increase in the infrared emission was obtained. In these excess cesium cathodes there is also an appreciable increase in the  $(F_1-F_2)$  response so that during the cooling process the increase in sensitivity is not related entirely to a shift of the response curve maximum toward the infrared. The spectral response is shown in Fig. 95. The (Cs/O) ratio for the cathode, obtained by count of the cathode, was 1.59 while that obtained from the flow measurement was 5.06.

For the tube fabrication conditions used it was not possible to obtain a surface for which the (Cs/O) cathode ratio exceeded 2.0 by a significant amount. The cathode versus flow (Cs/O) ratios, as shown in Fig. 96, do not fall on a smooth curve as was observed at 190°C. This might be

FIG. 91. THERMIONIC EMISSION.  
TRACER TUBE 1588-180.  
150°C.







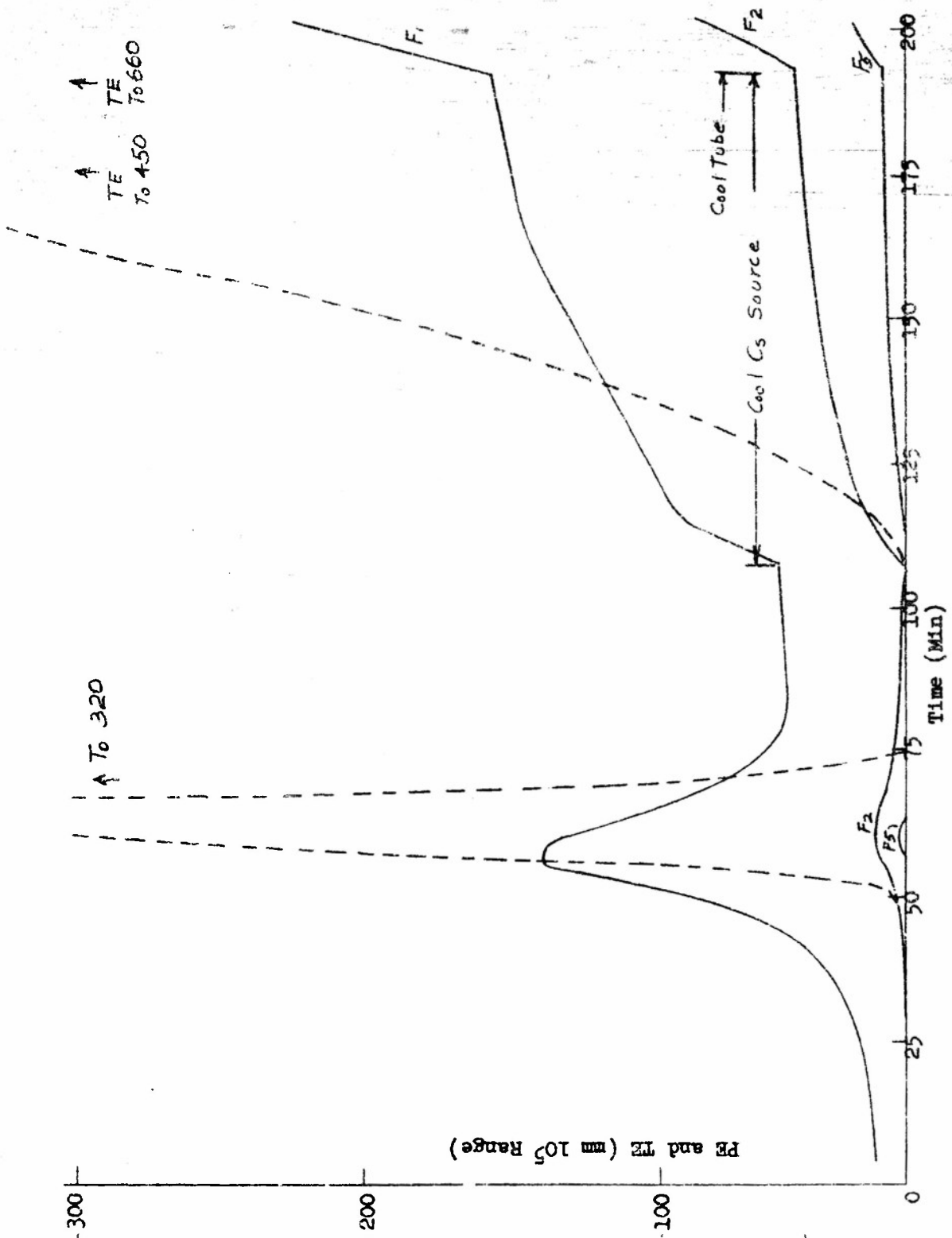
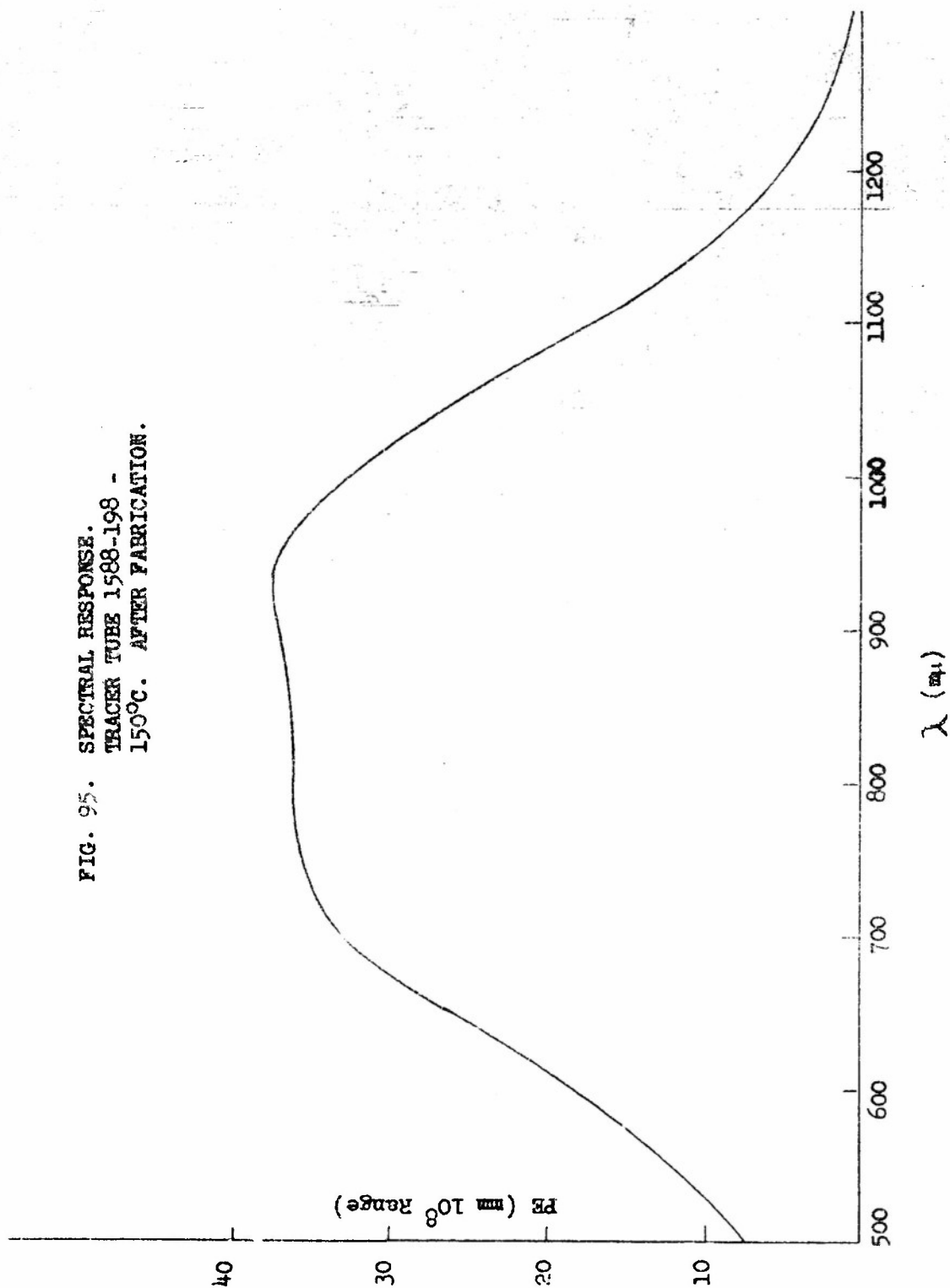


FIG. 94. THERMIONIC EMISSION AND OVEN SPECTRAL DATA. TRACER TUBE 1588-198 - 150°C.



FIG. 95. SPECTRAL RESPONSE.  
TRACER TUBE 1588-198 -  
150°C. AFTER FABRICATION.



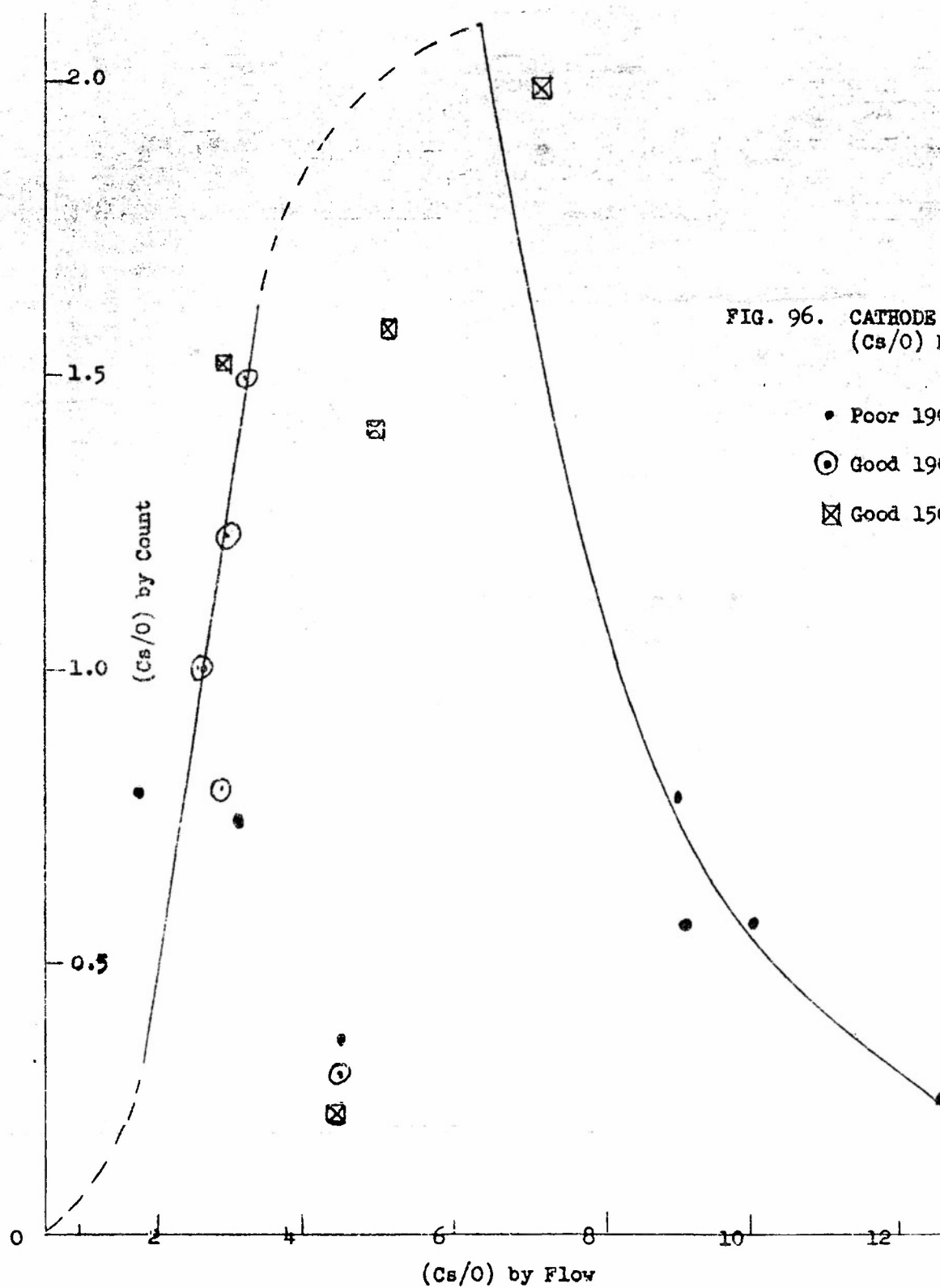


FIG. 96. CATHODE VERSUS FLOW.  
(Cs/O) MOLE RATIO.

due to the small amount of data obtained or to differences in processing. The spectral response curves, on the other hand, do indicate that excess cesium has not been completely removed. Comparison of the cathode (Cs/O) ratios with those obtained by flow show that considerable proportions of the added cesium collect elsewhere than on the cathode.

#### 4.14 Interpretation of tracer composition data

In the present section we wish to interpret the results of the two preceding sections and to correlate the data with the results of Section 3 and especially Section 3.1.

The first, and most obvious, fact which requires explanation is the maximum in the graph of cathode (Cs/O) ratio against the (Cs/O) ratio for the photocell (see Fig. 87). According to this figure, the addition of cesium beyond a certain point results in a loss of cesium from the cathode. This might be accounted for in a number of ways, three of which are as follows. (1) From the cesium-oxygen phase diagram the addition of cesium to  $\text{Cs}_2\text{O}$  results in the formation of a liquid solution of  $\text{Cs}_2\text{O}$  in cesium. This liquid solution might spread over not only the cathode but also the support wires and the tube envelope. This constitutes transport by capillary action. (2) It is known that under certain conditions a surface layer may possess mobility in two dimensions (surface gas) and hence spread rapidly in such a way as to establish equilibrium by transporting material to the tube supports and to the wall. This constitutes transport by surface flow. (3) Finally the possibility exists that a volatile compound is formed when cesium is added to  $\text{Cs}_2\text{O}$ . There is no such stable solid compound at  $190^\circ\text{C}$  but some species (such as  $\text{Cs}_3\text{O}$ ) may be sufficiently stable to diffuse through the vapor phase. This mechanism constitutes transport through the vapor phase.

The experimental evidence strongly favors the third of the above mechanisms although the other two are not completely excluded. The first piece of supporting evidence comes from the Ag-O-Cs cathode cesium vapor pressure study performed by Sayama<sup>21</sup>. He measured the cesium pressure in a phototube during the process of cesium addition and found it to be extremely low until the (Cs/O) ratio exceeded 2.0. Beyond 2.0 (Cs/O) the cesium pressure began to rise sharply, although remaining far below the vapor pressure of liquid cesium. Between 2 and 2.5 (Cs/O) the ionization gauge, used in the pressure measurements, behaved normally, i.e. in the

manner expected for cesium vapor. Beyond 2.5 (Cs/O) the gauge characteristics began to change. Sayama pointed out that the gauge behavior strongly indicated some other substance than cesium in the vapor and suggested  $\text{Cs}_2\text{O}$  as a possible species. This study, it is worthwhile to note, was performed at  $1450^\circ\text{C}$ .

The third hypothesis is further supported by some experiments performed by Dr. Khi-Ruey Tsai which conclusively demonstrate that oxygen transport may accompany cesium transport. Dr. Tsai found that if a small closed tube containing  $\text{Cs}_2\text{O}_2$  at the bottom end is partially immersed in a hot bath ( $120^\circ - 1300^\circ\text{C}$ ) that cesium collected at the cool end and  $\text{Cs}_2\text{O}$  was left at the hot end. However, during this process a thin layer of solid  $\text{Cs}_2\text{O}$  formed above the bath surface. Actually there was a continuous film of oxide extending from the  $\text{Cs}_2\text{O}$  in the bottom to slightly above the bath surface. These oxides showed a gradation of colors from dark red to yellow. A clear region of glass remained between the yellow deposit and the cesium at the top. The identity of the remaining phase was conclusively established as  $\text{Cs}_2\text{O}$  by means of x-ray diffraction powder photographs. In this experiment oxygen transport was shown to occur from the bottom to the region above the bath surface although the mechanism is not established.

In view of these supporting experiments it seems highly likely, (a) that transport occurs through the vapor phase, and (b) the moving species contain oxygen. Thus the data of Fig. 87 on cathodes prepared at  $1900^\circ\text{C}$  seem to be accounted for in a highly satisfactory way.

When we consider the experiments at  $1500^\circ\text{C}$  in the light of the above discussion several factors appear which require explanation. The first of these concerns the fact that cathodes prepared at  $1500^\circ\text{C}$  by introducing very large excesses of cesium into the phototube still have high infrared sensitivity while such cathodes prepared at  $1900^\circ\text{C}$  have very low infrared sensitivity. This is almost certainly due to differences in the baking operations in the two cases and to the differences in silver base. At  $1900^\circ\text{C}$  an ohmic conduction current appears at lower (Cs/O) ratios, for the phototube, than at  $1500^\circ\text{C}$ . This is very clearly shown by comparing Figs. 15 and 17 for cathodes prepared at  $1900^\circ\text{C}$  and  $1500^\circ\text{C}$  respectively. By the time, therefore, that cesium had been added to a photocell at  $1900^\circ\text{C}$  to such an extent that the (Cs/O) ratio was large the conduction current was so large that spectral response measurements were impossible. These tubes were usually not baked long enough for the conduction current to be reduced. This was the case, for example, for tube 1588-145 (see Figs. 88, 89, 90). A large

excess of cesium was added in this case and the conduction current was so large that it seemed, at the time, hopeless to bake the tube long enough to distill excess cesium from the cathode to the wall and to reduce the conduction current. We now know, of course, that this could probably have been done but at the time this did not seem evident. Another example is furnished by the tube, prepared at 190°C, corresponding to the peak point of Fig. 87. This tube, 659-33, passed through an intermediate stage of high infrared sensitivity as shown by Fig. 82. The tube was not baked, however, after stopping the cesium flow for a long enough period to restore infrared sensitivity by distilling cesium from the cathode. We now know that this could be done but this was not clear at the time the tube was prepared. Some of the tubes prepared at 190°C by adding large excesses of cesium were baked for considerable periods with the cesium source cool but these tubes were those prepared on thin silver bases (10,000A) and hence they did not develop infrared sensitivity for an entirely different reason. At 150°C, on the other hand, the high ohmic conduction currents did not develop until the (Cs/O) ratios were higher. Moreover, by the time these tubes were prepared it was known that infrared sensitivity could be restored to a tube containing even a large excess of cesium by prolonged baking. This was, therefore, done for the 150°C tubes and the final tubes had, as the result, rather high infrared sensitivities. In brief, the processing methods used in preparing the 190°C tubes were more uniform than those used on the 150°C tubes, chiefly because the preparation method was less well understood at the time. This probably contributes to the fact that the curve for (Cs/O) by count versus (Cs/O) by flow is smoother for the 190°C data than for the 150°C data.

In view of the fact that a smooth curve with a well marked maximum is not obtained at 150°C when (Cs/O) by count is plotted versus (Cs/O) by flow can we conclude that a volatile oxide is also formed at 150°C? The answer is that more careful inspection of the data strongly indicates the formation of a volatile oxide even at 150°C. The argument is as follows. In the first place the cathode (Cs/O) ratio for the 150°C tubes never exceeds 2.0 by more than experimental error no matter how much cesium is added to the tube. Moreover, the photocell to which the greatest amount of cesium was added, (Cs/O) by flow = 10.9, the cathode (Cs/O) ratio, 1.27, was lowest. Thus, although scatter in the data, due to variation in processing conditions, tends to obscure the maximum, the data are compatible with the view that the largest excesses of cesium tended to reduce the amount of cesium on the cathode. This tends to be supported by the fact (see Table XV) that the ratio of moles cesium on the

cathode to that on the backing disc shows a general tendency to decrease as the (Cs/O) ratio for the tube (obtained by flow measurement) increases. This ratio of cesium on cathode to that on the backing disc decreases from 650 to 41 for tubes fabricated at 150°C. These data are also consistent with the transport of cesium to the tube envelope by means of a volatile cesium oxide. We conclude, therefore, that even though Cs<sub>2</sub>O solid is stable at 150°C the solid probably has an appreciable vapor pressure.

It is also of interest to compare the results obtained in this section with those of Section 3.1. For the tubes described in Section 3.1 the maximum thermionic emission is obtained when the (Cs/O) ratios by flow are between 1.6 and 1.8. On the other hand, for the tracer tubes prepared at 190°C the (Cs/O) ratios (by flow) at maximum thermionic emission are larger. For example, in Fig. 81 the maximum comes at 2.9, in Fig. 84 at about 2.6, and in Fig. 88 at about 2.3. This difference is probably due in part to the different cathode areas relative to the tube envelope areas. For the tubes of Section 3.1 the cathode areas were approximately 22 cm<sup>2</sup>, and the area of the glass envelope approximately 113 cm<sup>2</sup>. For the tracer tubes of the present section, however, the cathode areas were 2.86 cm<sup>2</sup> and the glass envelope areas approximately 80 cm<sup>2</sup>. The ratio of envelope area to cathode area is 5 and 26 respectively in the two cases. If, therefore, cesium reacts with the glass envelope to the same extent in the two cases we might expect that the proportion of cesium on the wall as compared to cesium on the cathode would be only one fifth as great for the tubes of Section 3.1 as for those of the present section. The proportion of cesium on the wall to that on the cathode for tracer tubes prepared at 190°C is shown by the following table. The data are taken from Table XIV.

Tube	(Cs/O) Flow	(Cs/O) Count	<u>Cesium on Wall</u> <u>Cesium on Cathode</u>
8	2.23	1.01	1.21
15	2.79	1.49	0.88
16	2.51	0.80	2.14
17	2.26	1.23	0.87
ave.	2.45	1.13	1.27

The proportion of cesium on the wall to cesium on the cathode was computed by using the fact that the (Cs/O) ratio by flow gives the total cesium entering the tube to oxygen on the cathode. All of the above tubes were prepared by adding cesium until maximum thermionic emission was approxi-



mately reached. If we suppose that the amounts of cesium per unit area on the wall and cathode respectively are the same for these tubes as for the tubes of Section 3.1 at comparable stages of processing then we conclude that the proportion of cesium on the wall to that on the cathode for the tubes of Section 3.1 is approximately 0.25 at the same stage. If we use this figure to correct the data of Section 3.1 so as to obtain the cathode cesium to oxygen ratio we find for this ratio 1.28 to 1.43 at maximum thermionic emission. This is still higher than the cathode (Cs/O) ratio of 1.13 found for the tracer tubes prepared at 1900°C but the discrepancy is reduced. The agreement is probably as good as can be expected since we have assumed that cesium is uniformly distributed over the glass envelope of the tube. This is probably not a valid assumption since the glass used in making metal to glass seals for introduction of the lead wires in the tube is not the same as for the remainder of the envelope and differences in the rate of reaction with cesium are to be expected. This point can be checked by making use of the data obtained on the backing disc by determining the activity of the disc with a Geiger counter. The ratio of the number of moles of cesium on the cathode to that on the backing disc is given in Table XIV. Assuming that the same amount of cesium per unit area is on the tube envelope as on the backing disc these data can be used to calculate the ratio of cesium on the wall to that on the cathode. If this is done for the same four tubes as those above the following results are obtained. The amount of cesium on

Tube	Cesium on Cathode Cesium on Disc	Cesium on Wall Cesium on Cathode (Calculated)
8	39.5	0.66
15	52.52	0.50
16	22.68	1.15
17	50.62	0.71
	ave.	0.71

the wall compared to that on the cathode has the same order of magnitude as the measured value computed above from (Cs/O) count and (Cs/O) flow but is lower by an amount which exceeds experimental error. This can only mean that the glass envelope of the tube reacts with more cesium per unit area than does the glass backing disc. This becomes even more pronounced when large excesses of cesium are introduced into the tubes. Consider for example tube 18 of Table XIV. The (Cs/O) ratio by flow for this tube is 7.91 while (Cs/O) by count is 0.57. The ratio of cesium on wall to cesium on the cathode obtained from these figures



is 12.8. On the other hand, for tube 18 the ratio of cesium on cathode to that on the backing disc is 6.99. If we assume that cesium per unit area on the wall is the same as that on the backing disc we obtain (cesium on wall/cesium on cathode) 3.7. There is more than three times as much cesium on the wall than would be expected if the amount of cesium per unit area reacting with the wall is the same as for the backing disc. This means that either the wall is uniformly more reactive than the disc or, more likely, that some portion of the wall such as the glass in the vicinity of a metal to glass seal is more reactive. We must also remember that the backing disc has been more thoroughly cleaned than the tube envelope. Although the whole tube was thoroughly outgassed by heating to 400°C before preparing the photocell this would only remove volatile impurities. A thin layer of a nonvolatile impurity on the tube envelope would not be removed by this procedure and such an impurity may well react with cesium. The glass backing disc; on the other hand, was thoroughly cleaned by chemical methods before mounting in the tube envelope and was outgassed in addition. This may be a significant factor. In this connection it is of some interest that the tubes of Section 3.1 were more thoroughly cleaned. For the cathode was etched with dilute nitric acid and rinsed with distilled water before preparing the photocell. Thus both cathode and tube envelope were chemically cleaned before the outgassing operation. Moreover, several of the tube envelopes of Section 3.1 were used over and over again so that the tube walls no doubt became saturated with cesium. Under these conditions less cesium may have reacted with the wall during preparation of these cathodes. Considering all of these facts the agreement between the data on the tracer tubes and those of Section 3.1 is probably as good as can be expected.

As stated above, the amount of cesium found on the glass wall in the present section is, for tubes prepared to maximum thermionic emission, 1.27 times that on the cathode. This is roughly the same as was found by Prescott and Kelly<sup>18</sup>. However, the cathode (Cs/O) ratio obtained by the tracer study is 1.13. This is the average for four tubes. Prescott and Kelly found 2.1 for this ratio. The difference is probably due to differences in preparation. Prescott and Kelly apparently added more cesium to their cathodes than was the case in the tracer study. The ratio found in the tracer study certainly does not, however, agree with the idea that the cathode consists only of Cs<sub>2</sub>O. In fact Cs<sub>2</sub>O<sub>2</sub> might seem at first sight to be indicated. However, Cs<sub>2</sub>O<sub>2</sub> is not found in the x-ray study described in

the next section so this view can be excluded at once. It seems probable that two oxides of cesium are present in these cathodes one of which is  $\text{Cs}_2\text{O}$  and the other a higher cesium oxide, perhaps  $\text{Cs}_2\text{O}_3$  although a definite identification has not been made. If cesium had been added somewhat beyond maximum thermionic emission and the tube baked to restore infrared sensitivity the cathode (Cs/O) ratio would probably have been higher. For cathode 659-33 the cathode (Cs/O) ratio is 2.1, the highest obtained for any cathode. Unfortunately, this cathode was not baked long enough to restore infrared sensitivity although it seems very likely that this could have been done. If this had been done, however, a volatile oxide of cesium would have distilled from the cathode so that the (Cs/O) ratio by count would seem to be less than 2 even though the cathode might have contained only  $\text{Cs}_2\text{O}$ . This arises because of the loss of oxygen which is not taken into account in the calculation of the (Cs/O) ratios by count which appear in Table XIV, Fig. 87 and other places in this section. In view of this fact we might well ask how accurate is the (Cs/O) ratio of 1.13, obtained for cathodes prepared to maximum thermionic emission? This is hard to answer. Inspection of Fig. 87 suggests that the volatile cesium oxide is not formed until the actual cathode (Cs/O) ratio exceeds 2. However, we know that the cathode reactions are slow. If the rate of addition of cesium to the cathode is high then the pile-up of cesium at the cathode-vapor interface may produce a local excess of cesium beyond the ratio (Cs/O)=2. Under these conditions the volatile cesium oxide may be forming and distilling away even during the early stages of cesium addition in which the overall (Cs/O) ratio for the cathode does not yet exceed 2. Loss of oxygen from the cathode by such a process would make the (Cs/O) ratios, by way of count, of Table XIV lower than the actual (Cs/O) ratio for the cathode. This probably occurs to some extent but we do not think that this is a major factor for the following reason. Maximum thermionic emission is reached for the tubes of Section 3.1 before the (Cs/O) ratio for the whole tube becomes 2. Hence at maximum thermionic emission the cathode (Cs/O) ratio must have been less than 2 unless a very large proportion of the oxygen on the cathode had been removed in the form of a volatile oxide so that very little remained on the cathode. Nothing about the appearance of these cathodes suggests such behavior and hence, we conclude that the (Cs/O) ratio is actually less than 2 at maximum thermionic emission. Similarly the (Cs/O) ratio of 1.13 obtained in the tracer study is probably not much in error although it is conceivable that it might be low by a small amount.

In the case of tracer cathodes prepared at 1500°C the cathode (Cs/O) ratios for good infrared-sensitive tubes is considerably greater than the 1.13 obtained for the tracer cathodes prepared at 1900°C. This is probably due to the fact that, at 1500°C, cesium was added to well beyond maximum thermionic emission and the tube baked to restore infrared sensitivity.

It is evident from the above data that determination of the cathode (Cs/O) ratio is not sufficient to determine the compound formed in the cathode. In order to unambiguously identify the compound formed an x-ray diffraction study was undertaken as described in the next section.

#### 4.2 Cathode Phase Identification

One of the primary objectives of the Ag-O-Cs cathode investigation has been the determination of the actual phases present in the photosurface. This required the development of a method for the identification of solids in very thin films. Both electron and x-ray diffraction methods were considered. Electron diffraction has the advantage that even a thin film scatters sufficiently to provide an easily photographed diffraction pattern. The chief disadvantages are (a) that the electron beam may damage the specimen, and (b) that metal equipment is used with both the beam and specimen in the vacuum chamber thus increasing the chance of contamination. The problems associated with either introducing a prepared photosurface into an electron diffraction camera or fabricating the surface in the sample chamber are complex because of the reactivity of cesium and cesium oxides. The performance of definitive experiments would not be easy.

In the case of x-ray diffraction the situation is reversed. The specimen may be prepared in vacuo in a glass vessel and illuminated from the outside through a thin window. However, scattering from thin films is very small on direct x-ray illumination at right angles to the film, too small in fact to show up diffraction lines on films as thin as those of interest here even after a 48 hour exposure. Two methods of avoiding this difficulty were considered. The first involves illumination at glancing incidence. This seems feasible but troublesome to do with the readily available equipment. The second method involves scraping a sample from a considerable area and loading into a fine glass capillary tube with thin walls.

The capillary contents are then characterized by x-ray diffraction photographs. Application of the latter technique to the study of the oxide phases present in glow discharge oxidized thin silver films indicated clearly that the method could be used in the study of the actual photosurface. This method seemed by far better suited to the investigation and hence has been used.

Three types of cathodes have been studied by x-ray diffraction methods; namely, (a) good infrared-sensitive surfaces fabricated at 190°C, (b) cesium deficient (CsO) cathodes fabricated at 150°C, and (c) excess cesium cathodes fabricated at 150°C. The results of these investigations are discussed in the above order.

#### 4.21 Maximum thermionic emission - 190°C surfaces

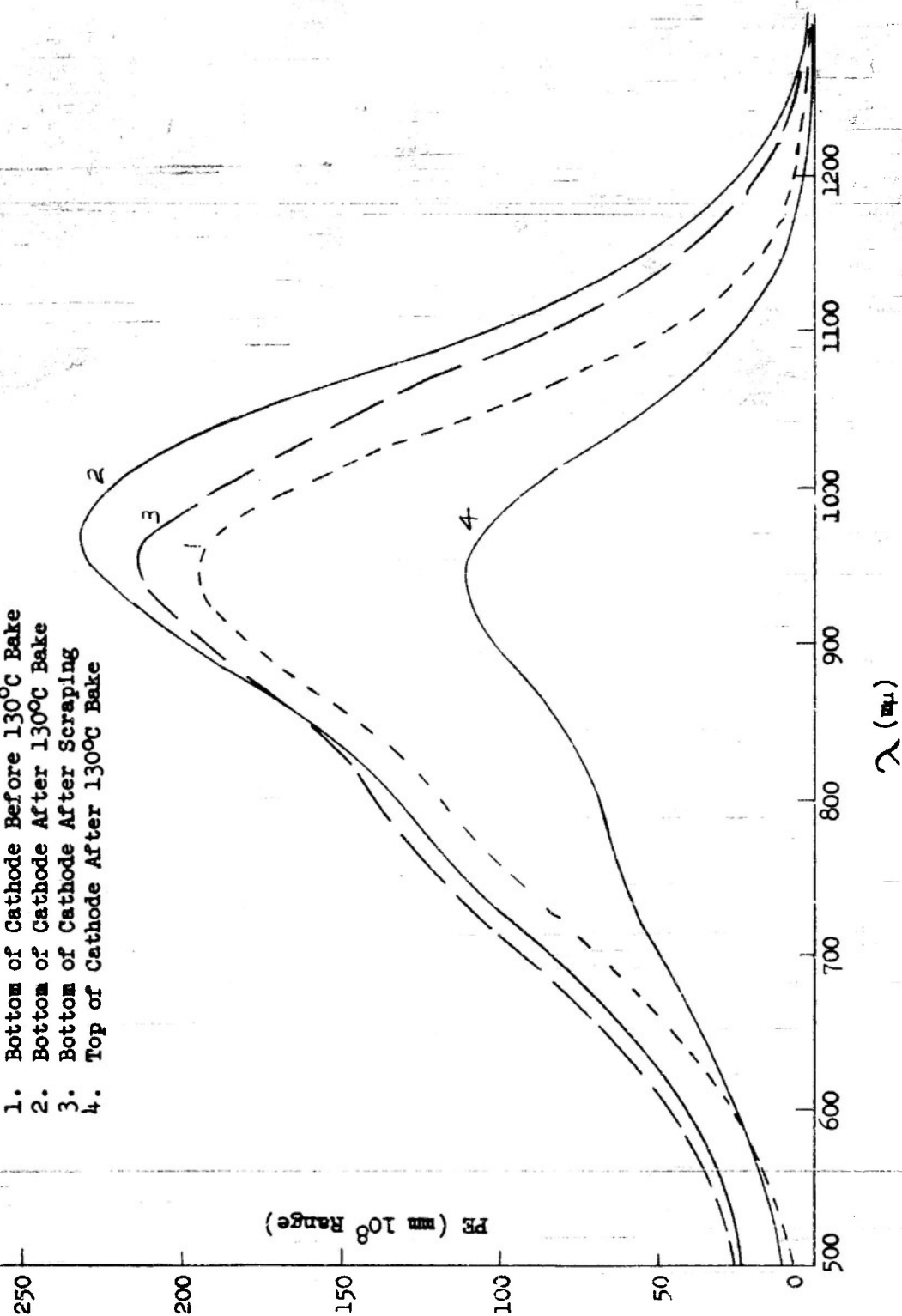
To determine the phases present in infrared-sensitive surfaces, prepared at 190°C to maximum thermionic emission, two phase identification tubes PT42 and PT55 were prepared. Tube PT42 was prepared on the vacuum system while PT55 was fabricated using the oven system of Section 2.12. The cesium was added in the case of PT42 to the thermionic emission maximum while in PT55 the addition was not discontinued until a stable 190°C surface was obtained. The tube designs used in these experiments have been described in Section 2.13.

The behavior of these cathodes during fabrication was typical of the 190°C tubes. During the oxidation step the silver was oxidized to a second order yellow in the case of PT42, and to a second order yellow red in PT55, corresponding respectively to the deposition of 1.94 and  $3.23 \times 10^{-5}$  gramatoms of oxygen. The changes in the spectral response during the processing are illustrated by the data for PT42 in Fig. 97. In the case of the cathodes to which cesium in excess of Cs<sub>2</sub>O was not added the photosensitivity at the top was less than at the bottom (Curves 1 and 4 Fig. 97). This difference has been attributed to a cesium molecular beam effect associated with the tube geometry (see Section 3.17).

The x-ray diffraction samples from the cathodes of tubes PT42 and PT55 were obtained by scraping the most sensitive regions of the cathodes. This process in the case of PT42 shifted the response as shown in Fig. 97. The small change in photosensitivity which occurred indicated

FIG. 97. SPECTRAL RESPONSE - PM42.

1. Bottom of Cathode Before 130°C Bake
2. Bottom of Cathode After 130°C Bake
3. Bottom of Cathode After Scraping
4. Top of Cathode After 130°C Bake





the removal of only a small fraction of the photosensitive species. In the scraping of PT55 the drop was more marked, actually the 960  $m\mu$  sensitivity was decreased from approximately 500 to 180 mm( $10^8$  range). The spectral responses of these cathodes did not change significantly in shape during the process of obtaining the x-ray diffraction photographs. A precise check was difficult because of the problems inherent in remeasuring the responses at exactly the same position with the equipment used. It is worthwhile to note that after scraping the cathode surface of both PT42 and PT55 the spectral response maximum was shifted to 940  $m\mu$  compared to 960 and 950  $m\mu$ , respectively, before scraping.

The x-ray diffraction and spectral response data for the 190°C tubes are given in Table XVI. The x-ray diffraction rings for the sample from PT55 were sharp and well defined. The diffraction rings for PT42, on the other hand, had a spotty appearance which indicates the presence of rather large  $Cs_2O$  crystallites. Intensities are estimated only for the rings from PT55. Interplanar spacings ( $d/n$ ) are given in Angstroms. The formula for the solid phase giving rise to each diffraction line is included in Table XVI together with the interplanar spacing for the pure substance. In the case of PT55 all of the lines are accounted for as due to either  $Cs_2O$  or silver. In the case of PT42 two weak lines at  $d/n=2.85$  and  $2.47$  are unidentified. The remaining lines for PT42 are accounted for as due to either  $Cs_2O$  or silver. Moreover, rather large crystals of  $Cs_2O$  are apparently formed.

It seems evident that  $Cs_2O$  is the dominant oxide phase in a highly infrared-sensitive cathode prepared to maximum thermionic emission at 190°C. We are unable to detect a higher oxide of cesium in these cathodes. Neither was any unreduced silver oxide found. The results of the preceding section show, however, that the cathode cannot contain  $Cs_2O$  alone since the cathode (Cs/O) ratio is substantially less than 2. The explanation for the failure to find the higher cesium oxide is probably as follows. The cathodes were not uniform due to the placing of the cesium capillary inlet relative to the cathode. Some areas of the cathode contain more cesium than others. Samples were taken, as explained above, from the areas having highest infrared sensitivity. These, however, are probably the areas containing the greatest proportion of  $Cs_2O$ . If the overall composition of an area were such that  $(Cs/O)=1.7$  and the oxides present were  $Cs_2O$  and  $Cs_2O_3$  then 90 mole percent of the mixture would be  $Cs_2O$ . A small amount of

TABLE XVI. TUBES PREPARED AT 190°C TO MAXIMUM THERMIONIC EMISSION AND USED FOR PHASE IDENTIFICATION BY X-RAY DIFFRACTION

COMPOSITION AND SPECTRAL DATA					
Tube	(Cs/O)Flow	Stage	Wavelengths (mμ)		Photocurrent at Maximum mm (10 <sup>8</sup> range)
			Maximum Photocurrent	Long Wave Limit	
PT42	*	After Fabrication	950	1055	195 (Bottom) 110 (Top)
		After 126°C Bake	960	1090	230 (Bottom) 110 (Top)
PT55	1.5	After Fabrication	960	1065	500
		After 130°C Bake	950	1065	500

\* In PT42 cesium addition was stopped at maximum thermionic emission.

X-RAY DIFFRACTION DATA				
PTL2 d/n	Radiation	d/n	Radiation*	Relative Intensity
3.43	β	3.46	β	0.2
3.38	α	3.43	α	5
		2.91	β	1
2.90	α	2.92	α	3
2.85	?	-	-	-
2.47	?	-	-	-
2.36	β	2.37	β	5
2.36	α	2.36	α	10
2.13	α	2.12	α	1
2.05	β	2.05	β	0.5
2.04	α	2.04	α	4
1.90	α	1.98	α	1
		1.73	α	1
		1.46	β	-

\* Unfiltered x-radiation from a copper target tube was used. The symbols α, β represent lines arising from the K<sub>α</sub> and K<sub>β</sub> lines of copper. See Section 2.33 for experimental details.



$\text{Cs}_2\text{O}_3$  might escape detection. There is another factor which also makes the detection of  $\text{Cs}_2\text{O}_3$  difficult.  $\text{Cs}_2\text{O}$  is probably the outermost phase so that any  $\text{Cs}_2\text{O}_3$  crystals present are probably coated with a layer of  $\text{Cs}_2\text{O}$ . Since cesium compounds adsorbed  $\text{CuK}_\alpha$  radiation rather strongly the diffraction by  $\text{Cs}_2\text{O}_3$  would be weakened by the outer coating of  $\text{Cs}_2\text{O}$  and thus a small amount could escape detection.

#### 4.22 Cesium deficient 150°C photosurfaces

Since the thermionic emission maximum during cesium addition at 150°C occurs at approximately the same tube gross composition as at 190°C it was assumed that the phase identification results obtained at 190°C also apply to this surface. One marked difference between 190°C and 150°C tubes is the formation of a "stable" surface at low (Cs/O) ratios during fabrication at 150°C. During fabrication at 190°C, the decrease in emission which occurs on cooling the cesium source at low (Cs/O) ratios is considered to arise from the presence of unreduced silver oxide in the photosurface (see Section 3.1). To obtain more definitive data on the characteristics of tubes with low (Cs/O) ratios, a series of four x-ray diffraction tubes were prepared at 150°C with a final gross tube composition of (Cs/O)=1.0.

During the fabrication of the cathodes PT57, 59, 65 and 68 several interesting observations were made on the effect of the tube geometry on the photosurface formation. The three cathodes were oxidized in the glow discharge to give the following oxygen contents:

	<u>gramatom O</u>	<u>Color</u>
PT57	$1.95 \times 10^{-5}$	2nd order yellow
59	$3.36 \times 10^{-5}$	2nd order gold yellow
65	$2.57 \times 10^{-5}$	2nd order red green
68	$3.36 \times 10^{-5}$	2nd order dark green

On the addition of cesium to the photosurface it was observed that the color of the top half of the cathode was unchanged after sufficient cesium had been introduced to give a gross composition of (Cs/O)=1. The bottom half of the cathode, however, had changed to a grey black color while at the center there was a transition region of grey black fading into the oxide color. On cooling the cesium source at 1.0 (Cs/O) the thermionic and photoelectric emission rose to "stable" values. On cooling the tube to room temperature the photoelectric response increased, the

effect being most marked for the  $F_1$  and  $F_2$  responses. Thus the increase in response during cooling of these cathodes occurred predominantly in the wavelength region of less than 900  $m\mu$ . The spectral response of PT57 at the bottom (grey black), center (transition color), and top (yellow) of the cathode after fabrication, and after the equilibrating bake following cesium source seal off is shown in Fig. 98. It is worth noting in this surface that shapes of the spectral response curves of the cathode are to a rather large extent independent of the position illuminated though marked differences in the integral sensitivity occur. It is clear from Fig. 98 that the cathodes are quite non-uniform. This nonuniformity is more pronounced for cathodes with (Cs/O):1 than for any others which have been encountered.

The apparent decrease in the response at the cathode center on baking shown in Fig. 98 is not very significant because of the rapid change in response occurring in the color transition region. It is difficult to locate the same spot in remeasuring the spectral response. If the cathode had not been given an equilibrating bake before cooling to room temperature there would have been a more marked variation in response characteristics from top to bottom.

Since these cathodes represent good examples of cesium deficient tubes it is of interest to present the data in detail for PT59 and PT65. The tube PT59 exhibited a variety of response characteristics during processing which are typical of PT57, 59 and 68, whereas PT65 resembled the good infrared-sensitive tubes. In the tube assembly process small differences actually exist in the positioning of the cesium inlet tube relative to the photosurface and consequently it would not be anticipated that the actual photosurface formation conditions would be reproduced from tube to tube. It was not feasible to fix this variable in these tubes by repeatedly using the same envelope and capillary.

The behavior of the thermionic emission and the oven spectral response during the initial fabrication of PT59 is shown in Fig. 99. On cooling the cesium source there was a marked increase in the thermionic emission to a maximum followed by a decrease. Simultaneously, in this case, there occurred a marked decrease in the photoresponse. On cooling the tube to room temperature the photoemission increased primarily in the ( $F_1$ - $F_2$ ) region, indicating change occurring at wavelengths less than 900  $m\mu$ . After fabrication, the base region (grey black) of the

FIG. 98. SPECTRAL RESPONSE FT57

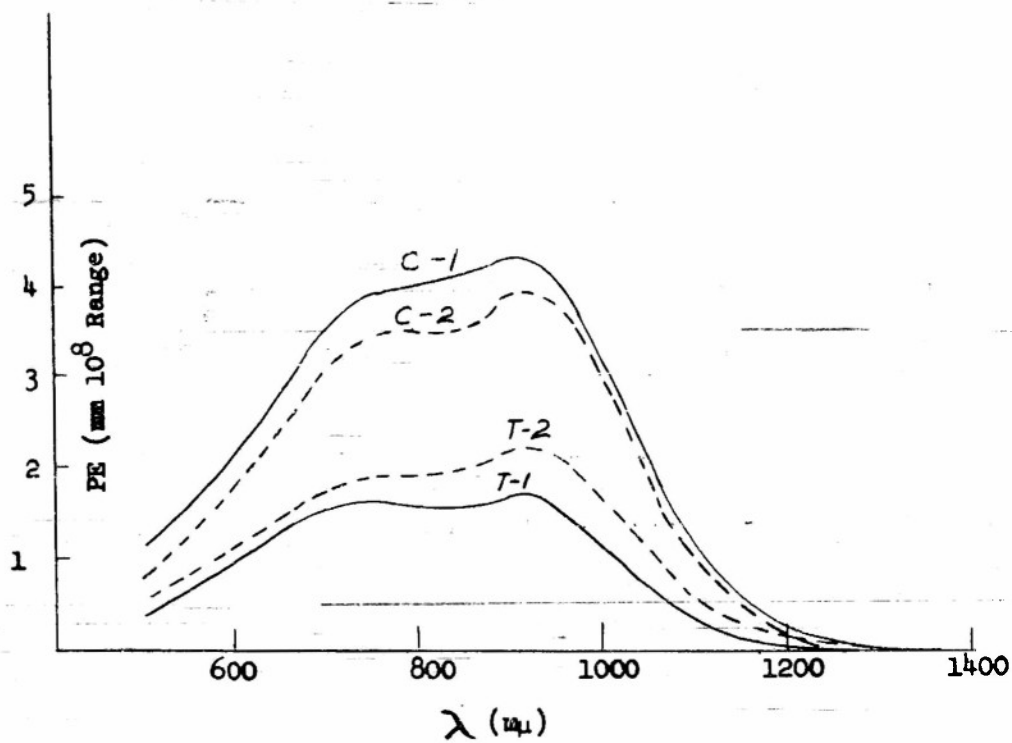
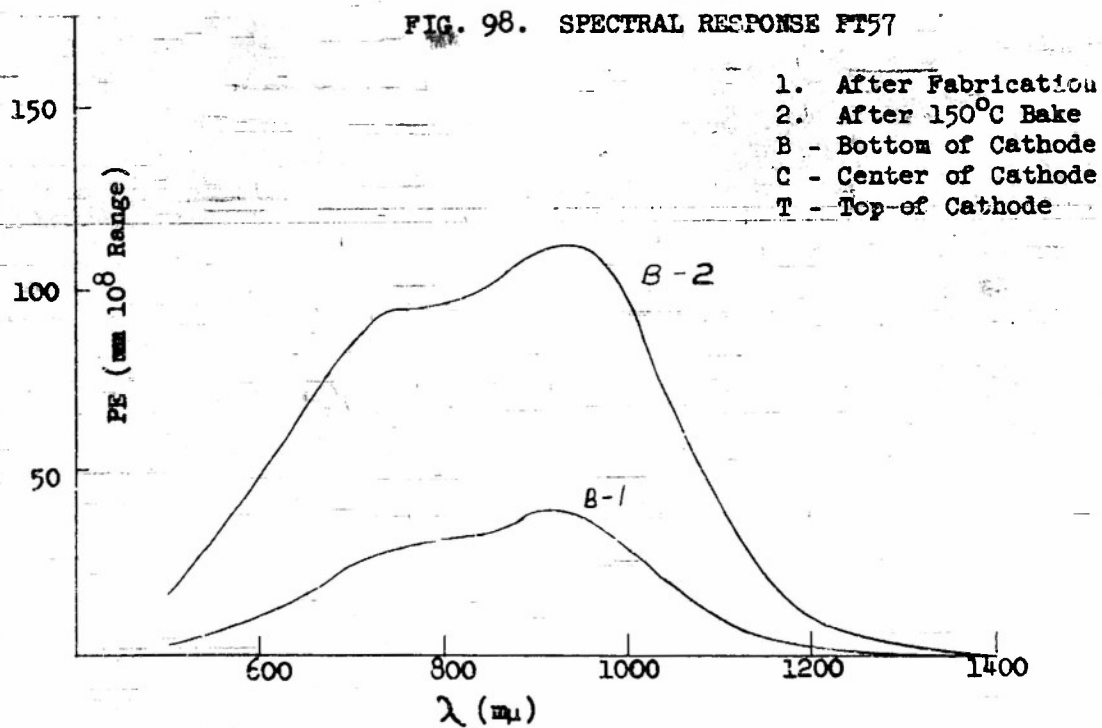
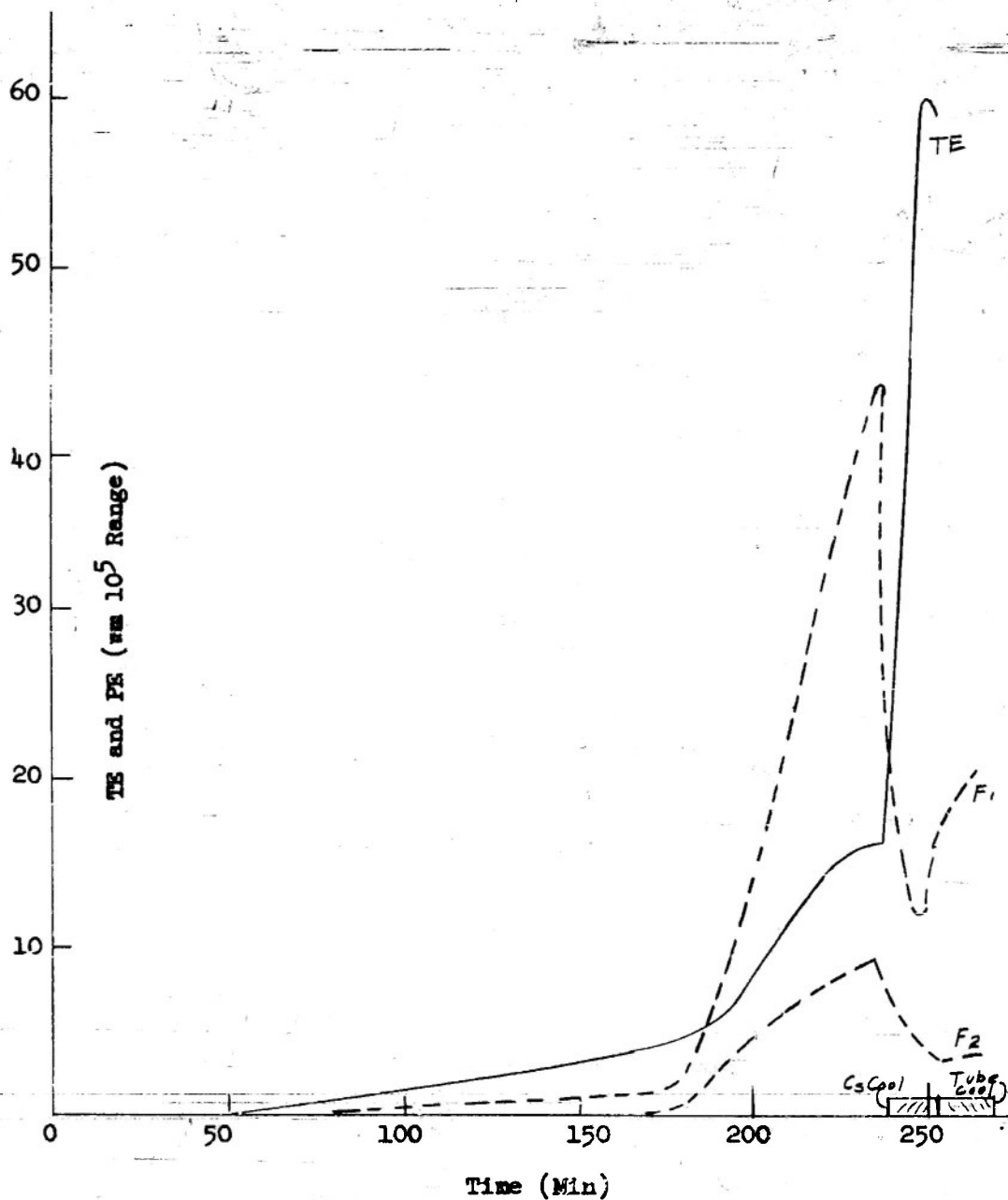


FIG. 99. INITIAL FABRICATION PT59.  
THERMIONIC EMISSION AND  
OVEN SPECTRAL DATA.

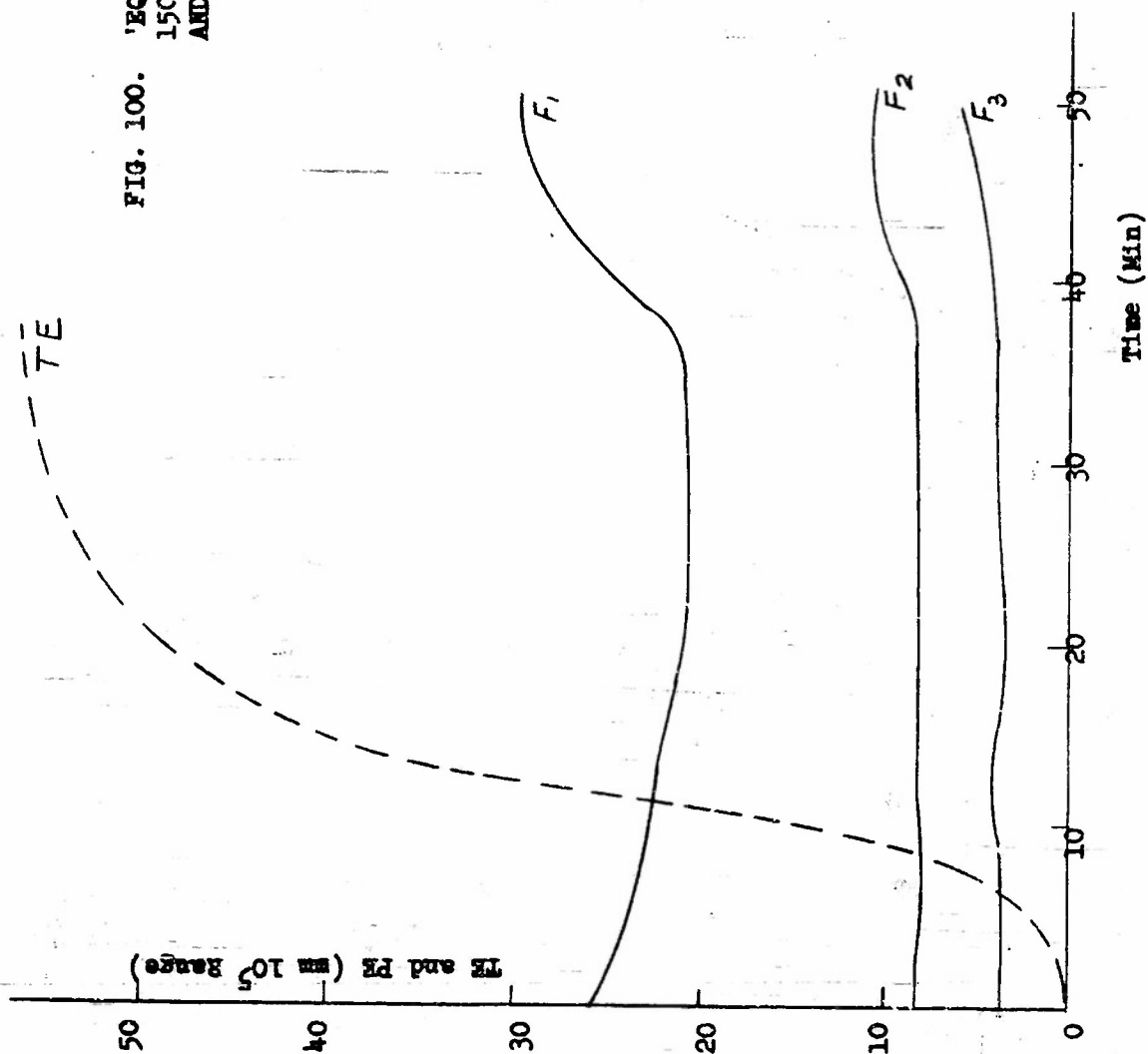


cathode exhibited a double maximum response as shown in Fig. 101. The responses at the other positions were similar in shape but with a marked reduction in the photoemission. After sealing off the cesium source the response at the bottom of the cathode corresponded to curve 2 in Fig. 101 while at the top of the cathode the response corresponded to curve 5. Thus the introduction of a small amount of cesium during seal off resulted in an elimination of the 700  $m\mu$  maximum.

During the equilibrating bake of PT59 at 150°C the thermionic and photoelectric emission became stabilized as shown in Fig. 100. Again on cooling the tube there was a marked increase in the ( $F_1$ - $F_2$ ) response. After the bake the spectral response at the bottom of the cathode corresponded to curve 3 in Fig. 101. In this case a definite maximum in the 900 - 1000  $m\mu$  region was developed. Scraping an x-ray powder sample from the cathode did not appreciably alter the response characteristics. Approximately three weeks later, after the x-ray diffraction experiments were completed, the spectral response at the bottom region had changed to a double peak curve as shown by curve 4 in Fig. 101. The cause of this shift has not been investigated. It is possible that the change is related to the slow decomposition of silver oxides present in this surface. A detailed study of the stability of cesium deficient surfaces over a long period of time was not performed.

The behavior of PT65 during the initial fabrication is illustrated by the data presented in Fig. 102. Cooling the cesium source in this case resulted in an increase in the thermionic and photoelectric emission to stable values. Cooling the tube resulted in an increase in both the ( $F_1$ - $F_2$ ) and  $F_5$  responses similar to that observed in the fabrication of 1.6 - 1.8 (Cs/O) tubes (see Section 3.1). The change in the tube characteristics during the equilibrating bake at 150°C is shown in Fig. 103. The spectral response characteristics after fabrication and after bake are shown in Fig. 104. During the baking operation the response at the cathode base did not change appreciably but a marked increase in the sensitivity at the top (red) portion of the cathode occurred. After scraping the central region of the cathode to remove an x-ray sample the spectral response at the base shifted to curve 3 in Fig. 104. No marked change in the response characteristics occurred during the following 3 day period in which x-ray photographs were prepared.

FIG. 100. 'EQUILIBRATING' BAKE PT59  
150°C. THERMIONIC EMISSION  
AND OVEN SPECTRAL DATA.



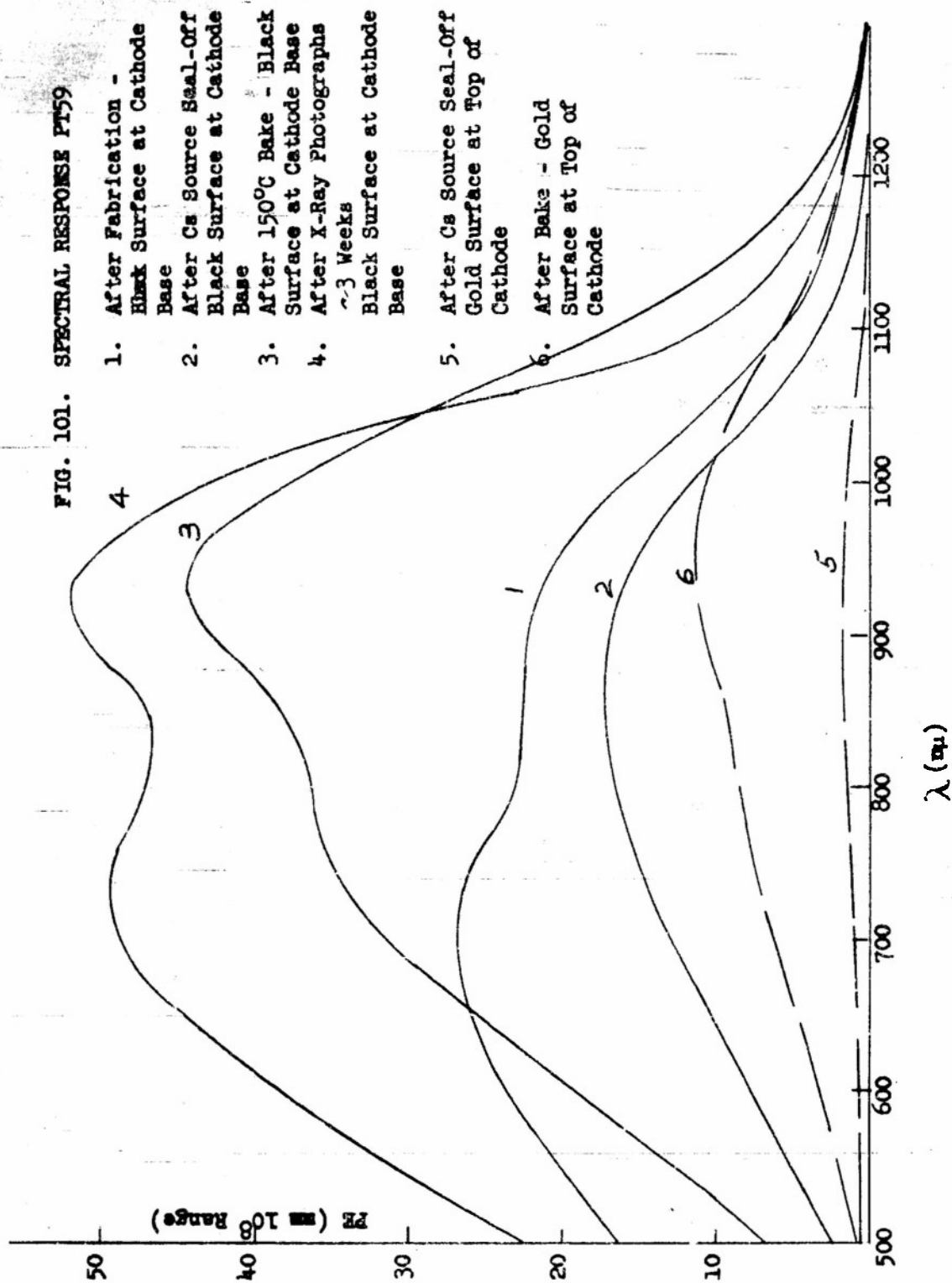




FIG. 102. INITIAL FABRICATION PT65 - 150°C.  
THERMIONIC EMISSION AND OVEN  
SPECTRAL DATA.

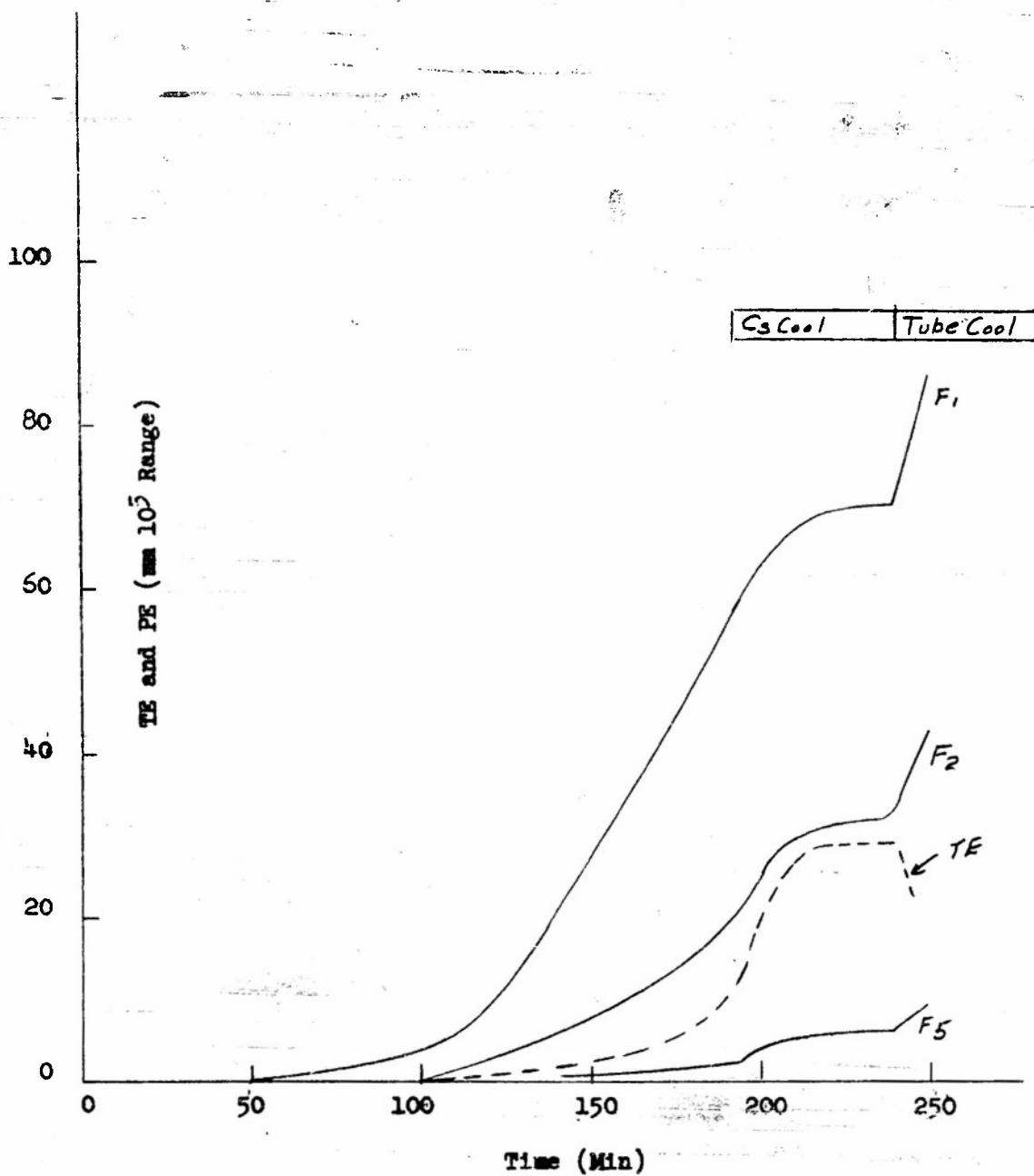


FIG. 103. 'EQUILIBRATING' BAKE PT65 - 150°C.  
THERMIONIC EMISSION AND OVEN  
SPECTRAL DATA.

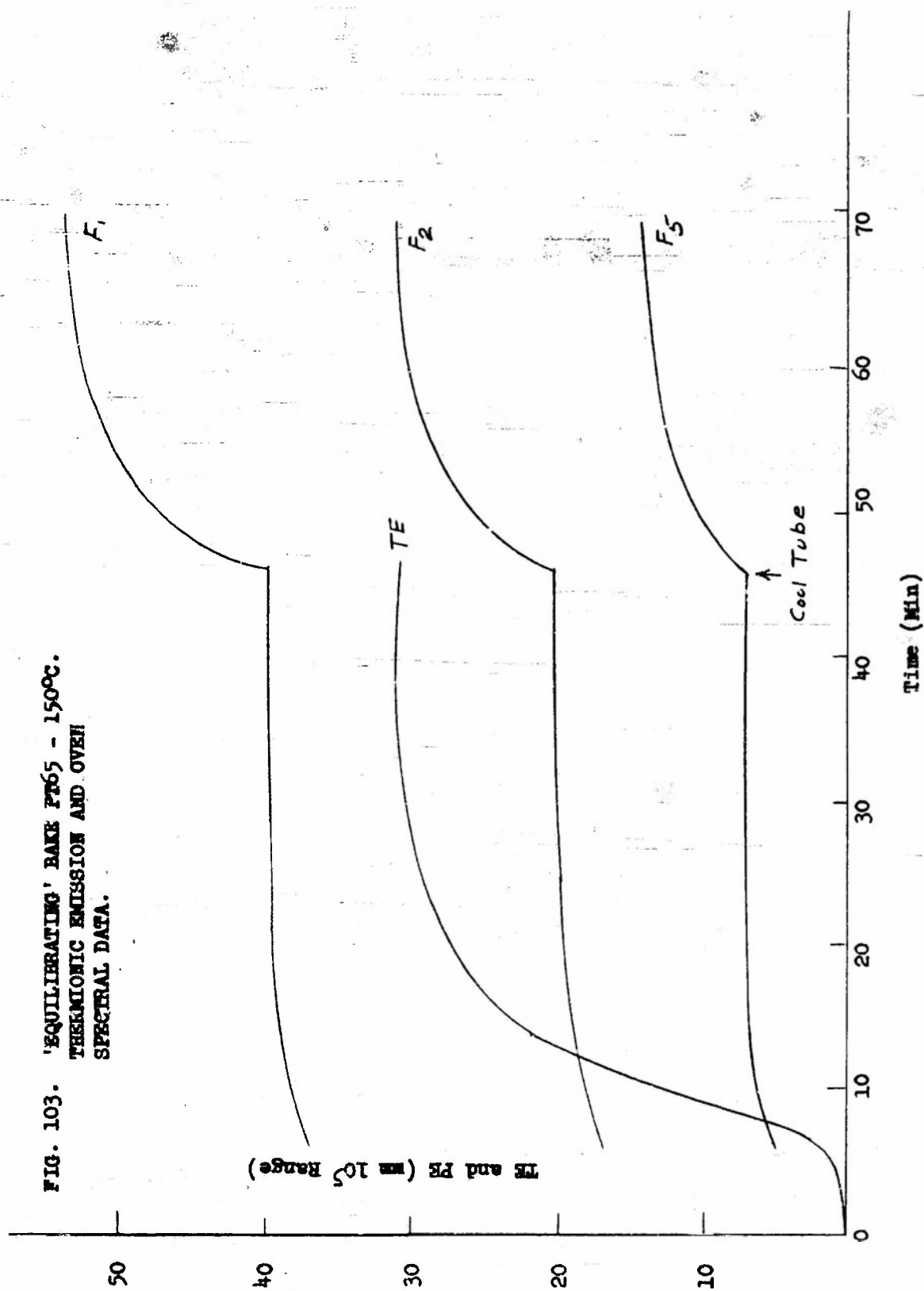
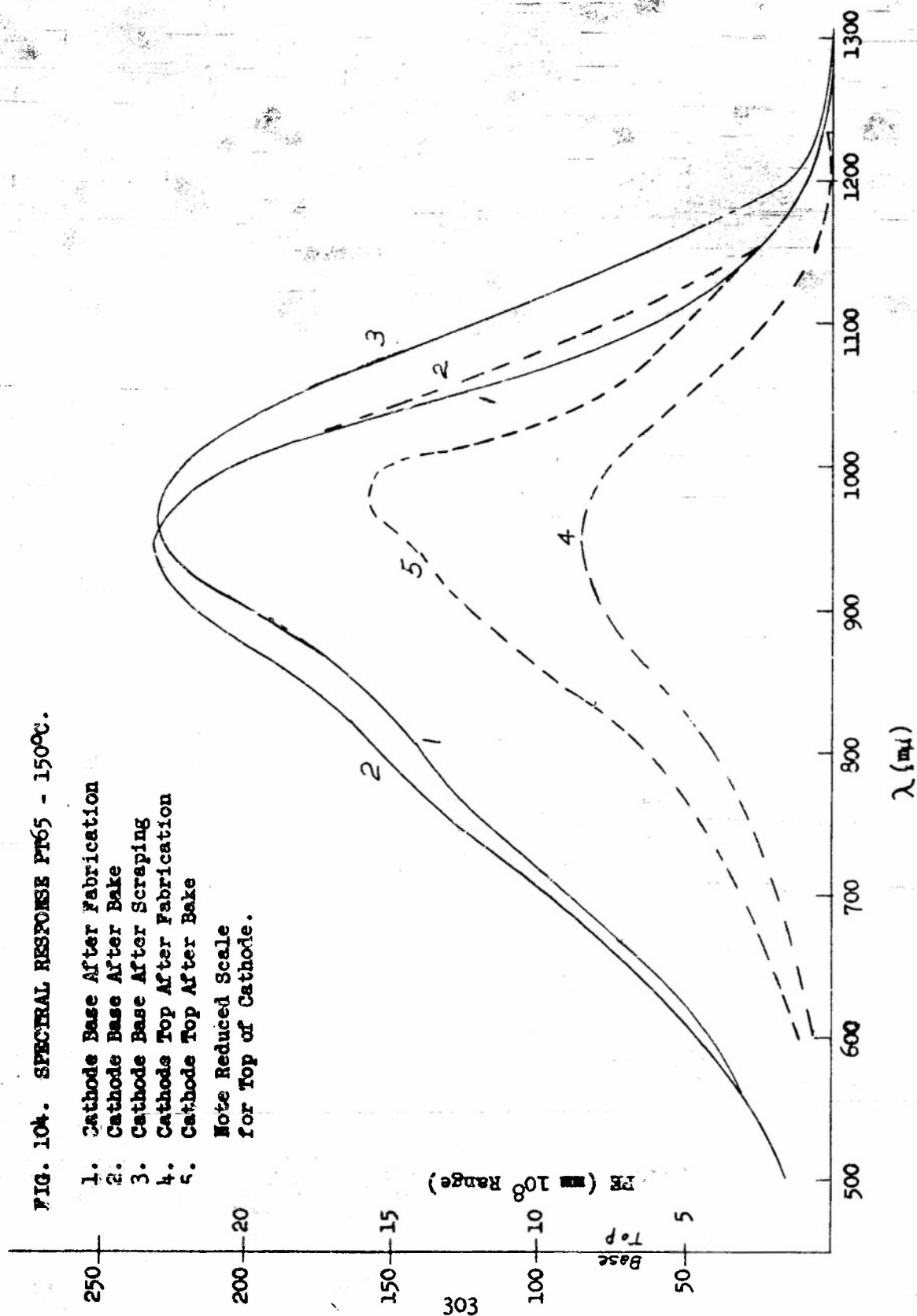


FIG. 104. SPECTRAL RESPONSE Pt65 - 150°C.

1. Cathode Base After Fabrication
2. Cathode Base After Bake
3. Cathode Base After Scraping
4. Cathode Top After Fabrication
5. Cathode Top After Bake

Note Reduced Scale  
for Top of Cathode.



The x-ray diffraction and spectral response data for PT59 and PT65 are summarized in Table XVII. The x-ray photographs for PT57 proved to be unsatisfactory due to a contamination of the sample by iron. During the initial oxidation and heat treatment of this tube the razor blade was appreciably oxidized. This oxide, on reaction with cesium, resulted in the formation of an iron film which did not adhere to the blade. Consequently the sample consisted primarily of iron and silver, the percentage of other phases being too small to detect. In the tubes with  $(Cs/O)=1$  it was difficult to obtain a sample in which there was a sufficiently high concentration of other phases, relative to the silver, to give characteristic diffraction lines which could be identified.

As shown in Table XVII the predominant constituent of the samples from PT59 and PT65 is silver. The sample in PT59 was removed primarily from the top, apparently unreacted region, of the cathode. In this case a pair of diffraction lines appear at 2.74 and 3.02Å. This pair of lines may be related to the  $CuK_{\alpha}$  and  $CuK_{\beta}$  reflections from the 2.72 line observed in the silver oxide pattern. The relative intensities of the other silver oxide lines are too low to be readily detected. Since the presence of lines with  $d/n > 3.1$  could not be readily established, because of the high background scattering, the phase responsible for the lines at 2.57, 2.52, 2.46, and 2.11 could not be uniquely assigned. The cesium oxides  $Cs_2O$ ,  $Cs_2O_3$ , and  $CsO_2$  do not have diffraction lines near 2.75Å and consequently the presence of silver oxide in PT59 is established.

For ease of comparison, the diffraction lines (with  $d/n$  between 3.0 and 2.0) for several oxides of cesium are given below.

$Cs_2O$	$Cs_2O_2(?)$	$Cs_2O_3$	$CsO_2$
$d/n(I)$	$d/n(I)$	$d/n(I)$	$d/n(I)$
2.91(100)	2.60(60)	2.64(80)	2.39(80)
2.64(1)	2.44(20)	2.47(10)	2.22(60)
2.18(3)		2.11(40)	2.14(60)
2.12(25)		2.02(20)	

The relative intensities are in each case referred back to the strongest line in each substance as 100. The intensities do not permit any comparison of the scattering power of one substance with that for a different substance. X-ray diffraction lines given for  $Cs_2O_2$  were not obtained by observation on the pure substance. Instead, these are lines found in a  $Cs_2O$  sample which had been exposed to a

TABLE XVII. CESIUM DEFICIENT PHASE  
IDENTIFICATION TUBES 150°C

Tube Data						
Tube (Cs/O) Flow	Stage	Max. PE $\lambda$ Long $\lambda$ Limit $\frac{1}{2}$ Max. PE $\lambda$ PE at Max.	m $\mu$	m $\mu$	m $\mu$	mm10 <sup>8</sup>
PT59	1.0 After Fab. After 150°C Bake	700/900 750/930	1250	1045	27/23	36/46
PT65	1.0 After Fab. After 150°C Bake	950 945	1250 1300	1050 1060	260 (Bottom) 815 (Top)	260 (Bottom) 16 (Top)

Diffraction Data <sup>1,2</sup>				
Interplanar Spacings		Phase		
PT59 d/n(I)	PT65 d/n(I)	Formula	d/n(I)	Radiation
3.02(1)		AgxOy	2.72(100) $\beta$	
2.74(2)		AgxOy	2.72(100) $\alpha$	
2.60(5)	2.62(5)	Ag(?)	2.36(100) $\beta$	
2.57(0.5)				
2.52(0.5)		AgxOy	2.51(25-50) $\alpha$	
2.46(4)	2.46(1)			
2.35(10)	2.35(10)	Ag	2.36(100) $\alpha$	
2.24(1)	2.24(1)	Ag	2.04(40) $\beta$	
2.11(1)	2.11(1)			
2.05(5)	2.05(5)	Ag	2.04(40) $\alpha$	

1. Background intensity too high to observe diffraction lines at  $d/n > 3.1$ .
2. The values of  $d/n$  for the diffraction lines of PT59 and PT64 were calculated using the wavelength for  $\text{CuK}\alpha$  radiation (1.54Å). In those cases in which lines actually arise from the diffraction of  $\text{CuK}\beta$  radiation the recorded  $d/n$  will be high by 10%. The values of  $d/n$  given for the various phases are the actual interplanar spacings in Angstrom units.

slight excess of oxygen. The above data are taken from Table II of Section 1.1, except that relative intensities have been changed to a scale of 100 as explained above.

Those diffraction lines given in Table XVII which cannot be identified as arising either from silver or from silver oxide are at  $d/n=2.57$ ,  $2.46$  and  $2.11$  for PT55 and at  $d/n=2.46$  and  $2.11$  for PT65. Since there is no line for either PT59 or PT65 at  $d/n=2.91$  it follows that the proportion of  $Cs_2O$  must be small. The line at  $2.46$  might be due either to  $Cs_2O_2$  or  $Cs_2O_3$ . The line at  $2.11$  might be due to  $Cs_2O_3$ . However,  $Cs_2O_2$  is not excluded because the diffraction lines for this substance are observed only as "extra" lines in impure samples of  $Cs_2O$ . Since  $Cs_2O$  has a line at  $2.11$  it cannot be told whether  $Cs_2O_2$  might also have a line at the same  $d/n$ . The line at  $2.60$  for PT59, at  $2.62$  for PT65, coincides with that expected for the  $\beta$  reflection from the  $2.36$  interplanar spacing of metallic silver. The intensities seem too high, however, for the line to be explained in this way. Some other phase is probably contributing.  $Cs_2O_2$  has a strong line at  $2.60$  and  $Cs_2O_3$  has a strong line at  $2.64$ . Either of these two oxides could be responsible for the intense lines at  $2.60$  and  $2.62$  respectively for PT59 and PT65. No decision can be reached at present between  $Cs_2O_2$  and  $Cs_2O_3$  as the oxide phase. As stated above, the samples are not well suited to the detection of oxide phases because of the large proportion of metallic silver.

The fact that  $Cs_2O$  could not be detected in PT65 is interesting since this cathode has high infrared sensitivity at the bottom portion. It seems likely that  $Cs_2O$  is present in small quantity. Because of the nonuniformity of the cathodes prepared to the ratio  $(Cs/O)=1$  the x-ray data are hard to interpret.

#### 4.23 Excess cesium 1500C photosurfaces

The preparation of cathodes at  $1500C$  which contain excess cesium is of particular interest in connection with the question of whether or not  $Cs_3O$  is a good infrared emitter. This question could not be settled by either the flow or tracer composition experiments in an unequivocal manner. Definitive results were obtained from the x-ray diffraction characterization of two excess cesium cathodes PT58 and 63.

In the fabrication of PT58, excess cesium was introduced at 150°C to a tube gross composition of approximately 2.4 (Cs/O). The cathode, after a 25 minute equilibrating bake at 150°C with the cesium source cool, developed a small  $F_2$  response which increased appreciably when the tube was cooled. The spectral response before and after the seal off of the cesium source is shown by curves 1 and 2 in Fig. 106. On baking the cathode at 150°C the thermionic emission and infrared sensitivity was recovered as shown in Fig. 105. After this bake the cathode exhibited appreciable infrared sensitivity as shown by curves 3 and 4 in Fig. 106.

In the fabrication of PT63 considerably greater care was exercised in the preparation of the tube for mounting on the vacuum system. After assembly, the tube was repeatedly rinsed with distilled water to remove any soluble materials which may have been deposited within the envelope during the assembly operation. It is important to note that the tube was rinsed with distilled water just before sealing to the vacuum system and beginning the fabrication process. Thus any film of soluble solid distilled onto the cathode or envelope is removed. During the fabrication of this cathode, excess cesium was introduced to give a tube gross composition of 2.8 (Cs/O). On baking the cathode for 40 minutes at 150°C, after cesium source seal off, no thermionic emission developed and the conduction current became stabilized at 0.6 mm( $10^5$  range) at 150°C. This did not significantly change the spectral response as shown by a comparison of curves 1 and 2 in Fig. 107. This cathode was then baked for an additional 125 minutes at 150°C and then cooled to 130°C and baked for another 200 minutes to facilitate the establishment of equilibrium in the photosurface. During this second bake the conduction current at 150°C was 0.62 mm( $10^5$  range) and decreased to 0.30 on cooling to 130°C. During the process of baking no appreciable  $F_2$  response was recovered. The  $F_1$  response at the end of the second bake was 127 mm( $10^5$  range) compared to 0.17 mm( $10^5$  range) for  $F_2$ . The response curves after these baking operations and the further processing of the surface are shown by curves 3, 4, and 5 in Fig. 107. It is apparent that the photosurface in this tube is characterized by a maximum response of 650 mμ and a long wavelength limit of ~850 mμ. The thermionic emission data for PT63 have already been discussed in Section 3.17 (see Fig. 27). The fact that the tube could be baked without restoring infrared sensitivity is probably due to the fact mentioned above, that the tube was rinsed with distilled water just prior to oxidation of the silver base. The tube walls, being clean, probably did not react with



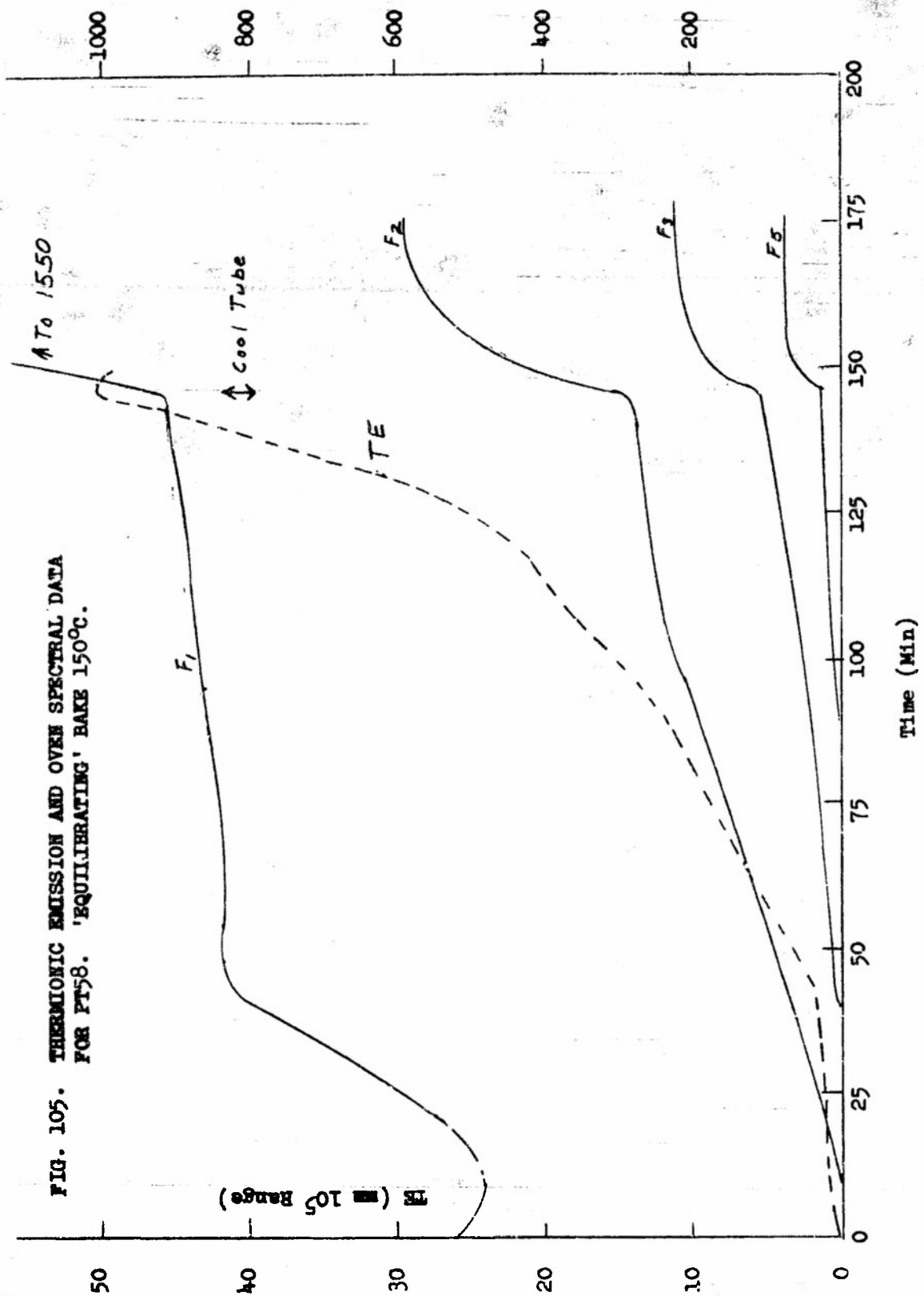


FIG. 105. THERMIONIC EMISSION AND OVEN SPECTRAL DATA FOR PT58. 'EQUILIBRATING' BAKE 150°C.

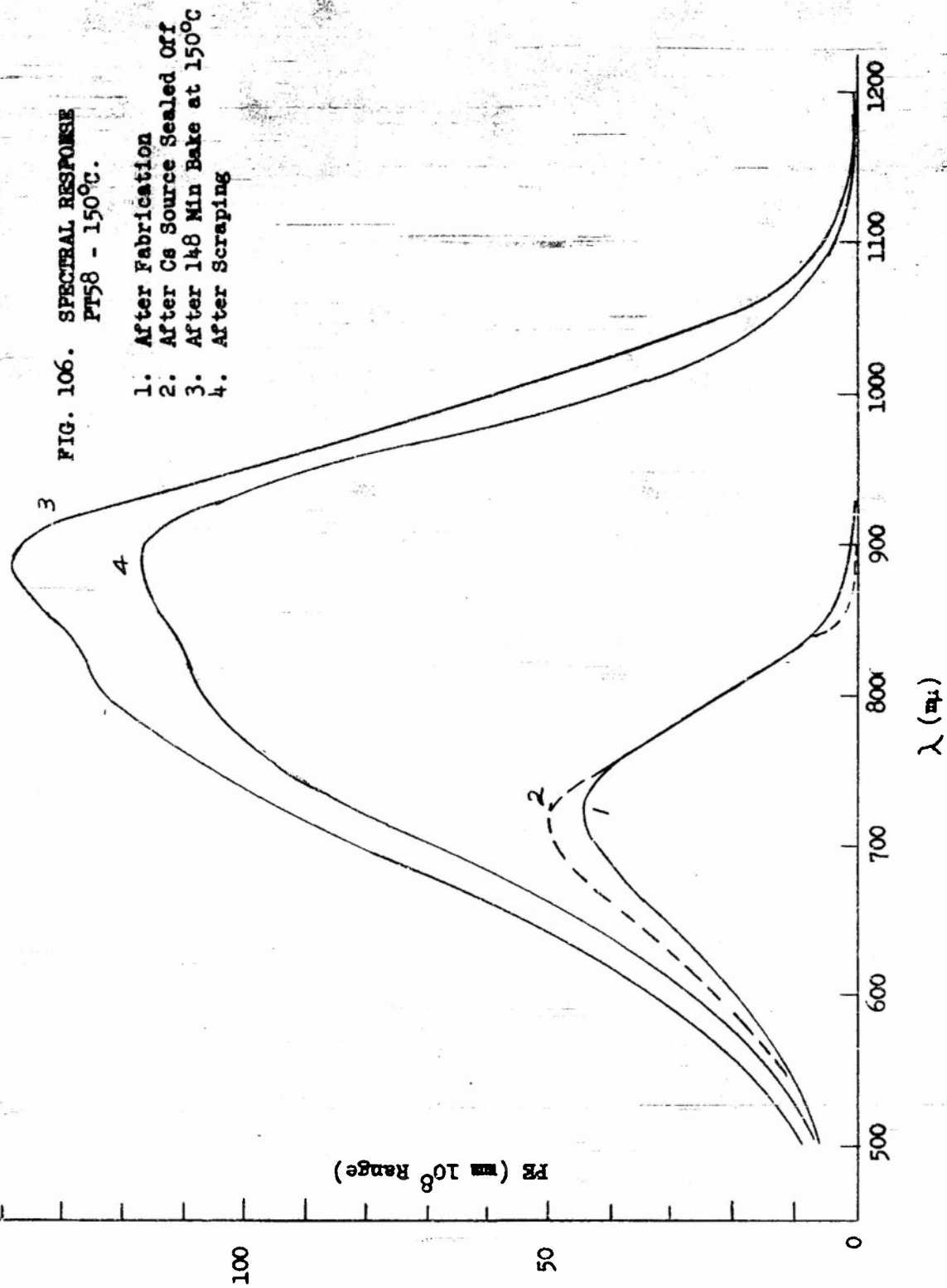
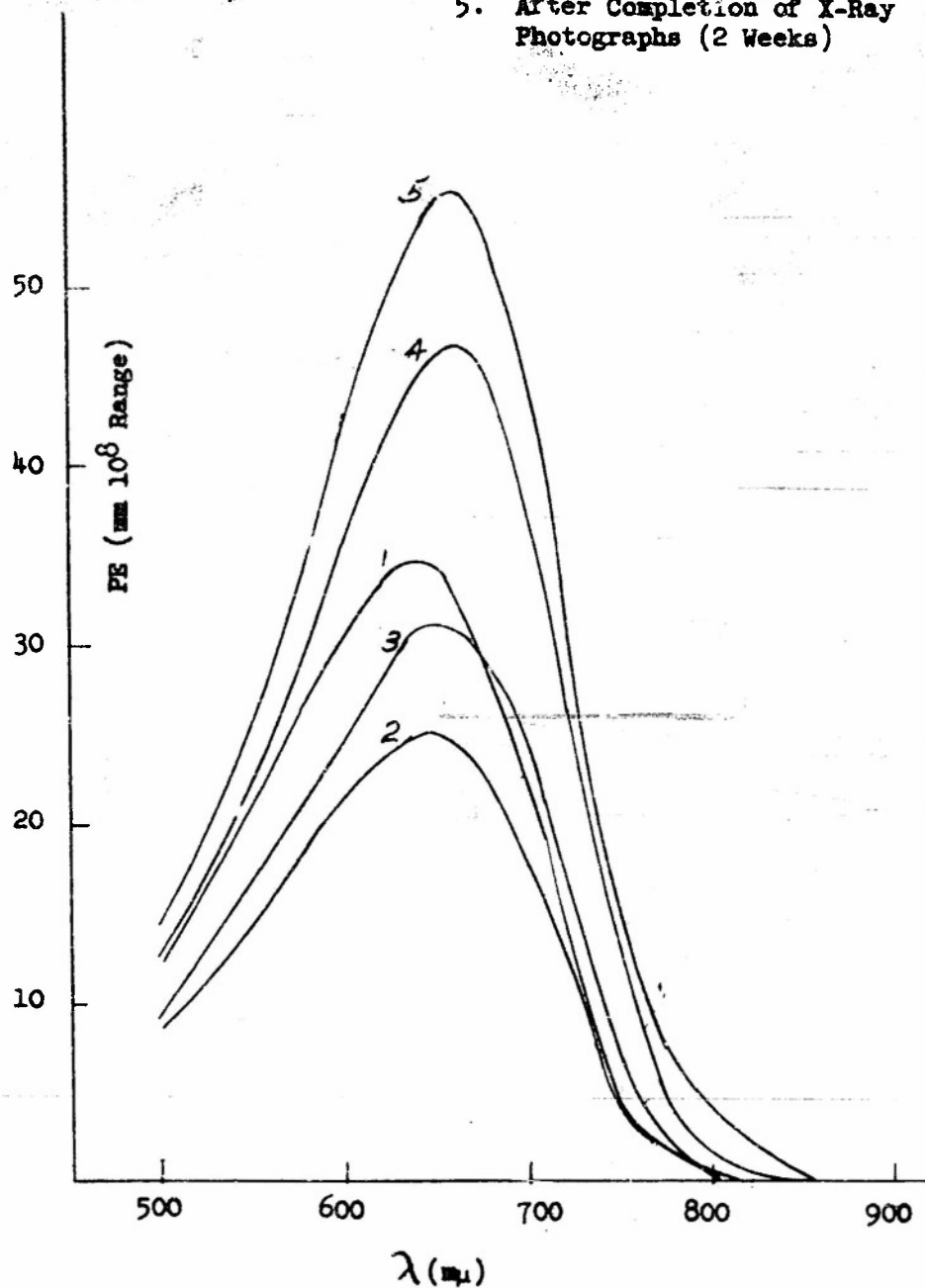


FIG. 107. SPECTRAL RESPONSE PT63

1. After Fabrication
2. After Bake 1, 40 Min - 150°C
3. After Bake 2, 125 Min - 150°C + 200 Min 130°C
4. After Scraping
5. After Completion of X-Ray Photographs (2 Weeks)



excess cesium.

The x-ray diffraction data are summarized for both photocathodes in Table XVIII. It is to be noted, as described in the table, that interplanar spacings were calculated from the line positions on the photographs using the wavelength (1.54 Å) for  $\text{CuK}_\alpha$  radiation. In some instances, due to the use of unfiltered radiation, the lines are actually due to diffraction of  $\text{CuK}_\beta$  radiation. In such cases the interplanar spacings,  $d/n$ , will be 10% too high. Since the x-ray diffraction photographs contain both diffraction rings, due to powder scattering, and spots, due to single crystal scattering, relative intensities are not reported. Included in Table XVIII are the interplanar spacings for the solid phases which produce diffraction lines at, or very near to, those which are observed. The interplanar spacings given for these substances are those actually observed for the pure substances. The radiation ( $\alpha$  or  $\beta$ ) diffracted from the planes, whose spacings are given, in order to produce the corresponding lines for the cathodes PT58 and PT63 is also indicated in the table. When the diffraction lines due to  $\alpha$  radiation from one set of planes coincides with the  $\beta$  radiation from another then the observed line may be a superposition of the two. An exception is the diffraction line at  $d/n=3.85$  for PT63. This is due to  $\text{CuK}_\alpha$  radiation. (See Section 2.33 for a description of the method of identifying reflections due to  $\text{CuK}_\beta$  radiation).

The powder diffraction pattern for PT58 unequivocally establishes the presence of  $\text{Cs}_2\text{O}$ . Since unfiltered radiation from a copper target x-ray tube was used to prepare the photographs, numerous single crystal diffraction spots appear as the reflection from crystals which were properly oriented. These spots for the most part arise from  $\text{CuK}_\alpha$  and  $\text{CuK}_\beta$  scattering as indicated by the Laue streak structure produced by the  $15^\circ$  oscillation of the sample. These spots are, in the case of PT58, associated with isolated crystals of  $\text{Cs}_2\text{O}$ . This is indicated by the fact that the strong  $\text{Cs}_2\text{O}$  lines, at  $d/n$  values of 3.43 and 2.91, exhibit a relatively high density of  $\text{CuK}_\alpha$  single crystal spots. Thus the single crystal reflection observed at 3.79 is to be associated with the  $\text{CuK}_\beta$  reflection from the 3.43 spacing of  $\text{Cs}_2\text{O}$ . There is no conclusive evidence for the presence of  $\text{Cs}_3\text{O}$  in PT58.

The powder diffraction pattern of PT63 unequivocally establishes the presence of both  $\text{Cs}_3\text{O}$  and  $\text{Cs}_2\text{O}$  in this cathode. The presence of a strong  $\text{CuK}_\alpha$  powder line at

TABLE XVIII. CESIUM EXCESS PHASE  
IDENTIFICATION TUBES  
150°C

Tube (Cs/O) Flow	Stage	Tube Data		Max. PEA PE at Max. mm10 <sup>8</sup>
		Max. PEA mμ	Long λ Limit mμ	
PT58 ~2.4	After Fab.	725	920	795 45
	After 150°C Bake	890	1200	985 138
PT63 ~2.8	After Fab.	640	800	715 35
	125 min. 150°C +200 min. 130°C	650	810	725 32

Diffraction Data

The interplanar spacings,  $d/n$ , are in Angstroms and were calculated, for PT63 and PT58, assuming the wavelength for the  $\text{CuK}\alpha$  line (1.54Å). In those cases in which the line is due to  $\text{CuK}\beta$  radiation the tabulated  $d/n$  will be too high by 10%. The interplanar spacings given for the possible phases are actual values for the pure solids. The type of radiation is indicated in each case. The letters S and P indicate single crystal spots and powder lines respectively. (See text for further explanation).

Interplanar Spacing		Possible Phases		
PT63	PT58	$\text{Cs}_2\text{O}$	$\text{Cs}_2\text{O}$	Ag
S+P 3.85(α)	S -3.79	3.80(100)α	3.43(100)β	
S+P 3.45	S+P -3.34-3.43	3.37(10)α	3.43(100)α	
P 3.17	P -3.19		3.16(25)α	
S 3.14		2.87(15)β		
S 3.00	S -3.02	2.68(50)β		
P 2.92	S+P -2.93	2.87(15)α	2.91(100)α	
	S -2.72			
S+P 2.62	S+P -2.63-2.59	2.68(50)α	2.64(1)α	2.36(100)β
S 2.53		2.54(2)α		
S 2.42	[S -2.44]	2.18(10)β	2.18(3)β	
S 2.38			2.13(25)β	
P 2.36	P -2.34			2.36(100)α
S 2.29		2.28(10)α		
P 2.27	P -2.27			2.04(40)β
	S -2.19		2.18(3)α	
S+P 2.13	S -2.13		2.13(25)α	
S 2.09	S 2.09	2.10(5)α		
P 2.04	P 2.04			2.04(40)β
S 2.01				
P 1.99			1.99(20)α	
S 1.92	S ~1.87	1.89(15)α		
P 1.81			1.80(10)α	
S 1.80	S 1.80		1.80(10)α	
P 1.76	S 1.77		1.76(20)α	

S = Single Crystal Spot.  
P = Powder Line

3.85A establishes the presence of  $\text{Cs}_3\text{O}$ . The three powder diffraction lines at 3.45, 3.175, and 2.92A exhibit the intensity distribution characteristic of  $\text{Cs}_2\text{O}$  and have an intensity comparable to the 3.85 line. In addition to the powder phases  $\text{Cs}_2\text{O}$ - $\text{Cs}_3\text{O}$  there are some rather large single crystals of  $\text{Cs}_3\text{O}$  present as indicated by the appearance of single crystal reflections superimposed on the  $\text{Cs}_3\text{O}$  powder pattern. If large single crystals of  $\text{Cs}_2\text{O}$  were present to an appreciable extent it would be anticipated that at least one reflection would be observed on the 3.17 or 2.92 lines as observed in PT58.

The x-ray diffraction results for the excess cesium cathodes provide several interesting conclusions. Considering the technique used in the processing of PT63 it would appear certain that phase equilibrium between  $\text{Cs}_2\text{O}$ - $\text{Cs}_3\text{O}$  was established. This surface is characterized by a maximum at 650  $\mu\text{m}$  and a long wavelength limit at 800 - 900  $\mu\text{m}$ . The fact that further cesium addition to this surface does not readily alter the response characteristics indicates that the response may validly be considered to be characteristic of  $\text{Cs}_3\text{O}$ . In addition the presence of large single crystals of  $\text{Cs}_3\text{O}$  in PT63 and  $\text{Cs}_2\text{O}$  in PT58 suggests that digestion of the surface in the presence of excess cesium may contribute to the formation of rather large single crystals. Supporting evidence for the occurrence of this process is provided by the observations made by Dr. Khi-Ruey Tsai on the preparation of single crystals of  $\text{Cs}_2\text{O}$  and  $\text{Cs}_3\text{O}$ .

It was pointed out in Section 3.1 that as cesium is added continuously to a photocathode the thermionic emission passes through a maximum when the  $(\text{Cs}/\text{O})$  ratio reaches about 1.7. At  $(\text{Cs}/\text{O})$  ratios beyond 2 the thermionic emission becomes very small. If, however, the addition of cesium is stopped beyond  $(\text{Cs}/\text{O}) \approx 2$  and the tube is baked for a sufficiently long period the thermionic emission rises and infrared sensitivity is restored. This might be due to the fact that cesium is removed from the cathode by reaction with the wall on baking and this hypothesis has been accepted throughout this report. It is also possible, however, that  $\text{Cs}_3\text{O}$  might be an infrared emitter which required prolonged heating for activation. The results on PT63 conclusively disprove this latter hypothesis since the tube was baked for considerable periods of time without ever developing infrared sensitivity. At the same time, the x-ray data show conclusively that the cathode contains  $\text{Cs}_3\text{O}$ . On the other hand PT58 is a tube to which excess cesium was added and which, on baking, recovered infrared sensitivity and in this cathode only  $\text{Cs}_2\text{O}$  could be conclusively identi-



fied. The implication therefore becomes strong that cesium was distilled away from the cathode on baking PT58 but not on baking PT63. We attribute this to the fact that PT63 was rinsed with distilled water just before sealing to the vacuum system. The tube was then outgassed at 400°C, in the usual way, and fabrication of the photocathode was begun. We believe that a thin layer of soluble solid was removed from the tube envelope during the rinse with distilled water. Tube PT58 was not treated in this way and hence the wall reaction with cesium was probably extensive.

The special treatment which was given to PT63 came about in an effort to improve uniformity of oxidation. It was observed during the course of sealing in the lead wires which support the cathode and provide electrical contact that a thin film of a white solid collected around the cool portions of the glass. The solid distills out of the tube in the subsequent outgassing at 400°C and it was thought that the substance had been removed from the tube. It was found, however, that oxidation of the silver sheet cathode was quite non-uniform and several oxidation-thermal decomposition cycles were necessary before uniform oxidation could be achieved. This was in contrast to the tubes described in Section 3.1 for which the cathode usually oxidized uniformly on the first trial. It was finally recognized, however, that in the tubes of Section 3.1 the same glass envelope, capillary, and cathode were used over and over by removing the oxides from the previous experiment by rinsing with dilute nitric acid and then with distilled water. The cathodes of the present section could not, however, be re-used. It was found by trial that the white solid, mentioned above, was water soluble so the tube was rinsed with distilled water just before mounting on the vacuum system. When this was done it was found, for several successive tubes, that the oxidation changed markedly. Uniform oxide coats were obtained on the first trial. Re-examination of the results of Section 3.1 also showed that difficulty with uniform oxidation was also occasionally encountered the first time that a new cathode and tube envelope were used but not thereafter. It seems likely that it is important to rinse the tube after the tube elements have been sealed in and the glass blowing, except for the final seal to the vacuum system, has been completed. The whole process developed in an effort to improve uniformity of oxidation. It was found, however, that tubes treated in this way, and to which excess cesium had been added no longer recovered infrared sensitivity on moderate baking. The implication is strong that a solid surface layer, which



could react with cesium, had been removed. The cathodes used in the tracer study of Section 4.1 were not treated in this way and hence the extent of reaction of cesium with the tube wall is probably greater than for PT63. It must be mentioned that reaction with the wall probably still occurs in a tube prepared in the manner of PT63. The reaction is, however, slower. It was observed in one case that infrared sensitivity could be restored by flaming the tube wall with a hand torch.

It is fortunate that a means was found to reduce the extent of the wall reaction since the data on PT63 then show conclusively that  $Cs_2O$  is not a photoelectric emitter in the far infrared even when subjected to prolonged heating at moderate temperatures.

#### 4.3 Chemical Composition and Spectral Response

It seems worthwhile at this point to briefly summarize the types of spectral responses which are obtained when photocathodes are prepared under various conditions. In most cases the conditions of preparation have been related to the chemical composition by methods described in previous sections of the report. Attention is restricted to massive cathodes since it is only in this case that the effect of silver base is reproducible enough to permit the effect of varying  $(Cs/O)$  ratio to clearly manifest itself in the cathode spectral response. The spectral responses listed below have not been corrected for dispersion or for lamp energy distribution, like the other spectral responses given in this report except in Section 3.2 where approximate correction for these factors has been made.

In order to indicate the relation between chemical composition and spectral response it is convenient first to consider the response for a photocathode prepared at  $190^{\circ}C$  by slowly adding cesium to maximum thermionic emission. Next we consider the spectral response of a cathode to which excess cesium has been added and finally the spectral response of a cathode which has been overbaked so that infrared sensitivity is lost.

At  $190^{\circ}C$  the maximum thermionic emission "stable" photosurface is obtained on the addition of cesium to a tube, of the same design as in Section 3.1, to a gross composition of  $1.5 < (Cs/O) < 2.0$ . On cooling the cathode to room temperature there is a marked increase in the infra-

red sensitivity for  $\lambda > 900 \text{ m}\mu$ . The spectral response of the final surface is characterized by a long wavelength limit of greater than  $1350 \text{ m}\mu$ , a photoemission maximum of  $950 - 990 \text{ m}\mu$  and a wavelength half maximum photocurrent of greater than  $1050 \text{ m}\mu$ . A typical response curve for this photosurface is shown by the solid curve of Fig. 108. It is observed experimentally that the magnitude of the photocurrent at the  $750 \text{ m}\mu$  inflection is variable relative to the emission at  $900 - 1000 \text{ m}\mu$ . This fact suggests that the surface contains two types of emitting centers contributing roughly in the manner shown by the two dotted curves in Fig. 108. Spectral response IA has maximum photoemission at  $950 - 990 \text{ m}\mu$  and a long wave limit of greater than  $1350 \text{ m}\mu$  while response IB has a maximum at  $750 \text{ m}\mu$  and a long wavelength limit of approximately  $1000 \text{ m}\mu$ . These response curves IA and IB correspond respectively to the Class I and II responses of Section 3.2 except that IA and IB have not been corrected for dispersion or lamp energy distribution.

X-ray diffraction studies of photocathodes prepared to maximum thermionic emission demonstrated that  $\text{Cs}_2\text{O}$  was the dominant oxide phase present (see Section 4.21). Considering the conditions under which the surface was formed it is reasonable to suppose (1) that cesium oxide  $\text{Cs}_2\text{O}$  is the surface phase and (2) that  $\text{Cs}_2\text{O}$  contains little if any excess cesium.

Since excess cesium was not introduced into the tube the photosurface must contain higher oxide phases than  $\text{Cs}_2\text{O}$ . This is indicated not only by the (Cs/O) ratio in the photocells obtained in Section 3.1 but also by the cathode (Cs/O) ratios obtained in Section 4.1. The observed differences in behavior during the fabrication of tubes at  $190^\circ\text{C}$  and  $150^\circ\text{C}$  and the tracer composition studies of this surface suggest that no appreciable silver oxide remains. The surface most probably corresponds to phase equilibrium between  $\text{Cs}_2\text{O}$  and  $\text{Cs}_2\text{O}_3$ . At a (Cs/O) mole ratio of 1.7 the surface would consist of 89%  $\text{Cs}_2\text{O}$  by volume which is equivalent to 90 mol percent  $\text{Cs}_2\text{O}$ . Under the conditions of fabrication used  $\text{Cs}_2\text{O}$  would be present as the surface layer while the  $\text{Cs}_2\text{O}_3$  would be an interior layer.

The addition at room temperature of very small amounts of cesium to this photosurface readily eliminates the IA response (see Section 3.41). On baking the surface at  $130^\circ\text{C}$  the infrared response is quickly recovered. This rapid recovery is due to the presence of the higher oxides in the photosurface. During the bake the excess cesium reacts

FIG. 108. PHOTOSURFACE I  
 $1.5 < (C_8/O)_{\text{Flow}} < 2.0$

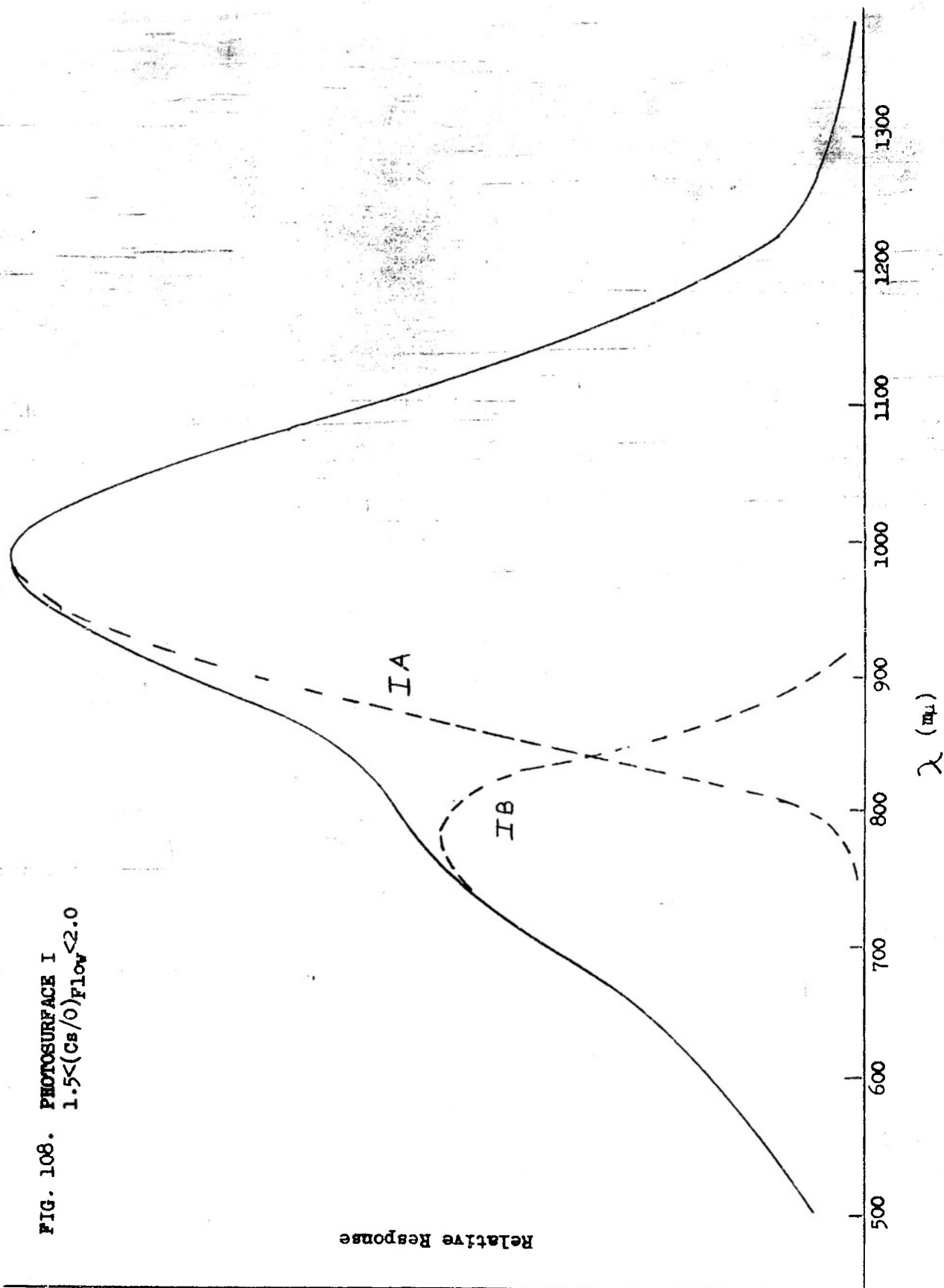
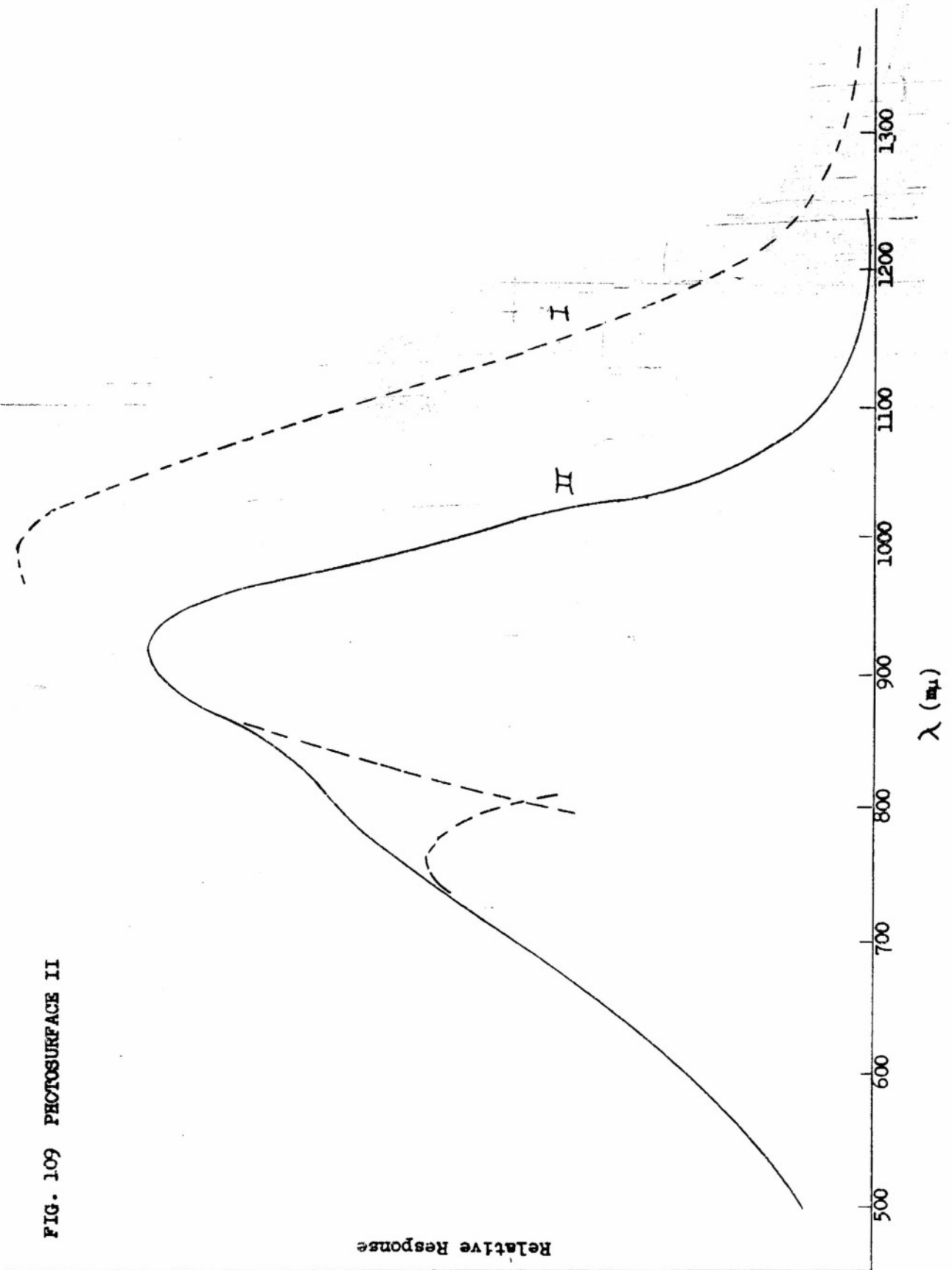


FIG. 109 PHOTOSURFACE II



with the  $\text{Cs}_2\text{O}_3$  to form more  $\text{Cs}_2\text{O}$ .

The excess cesium photosurfaces II, III, and IV, are characterized by the following response characteristics:

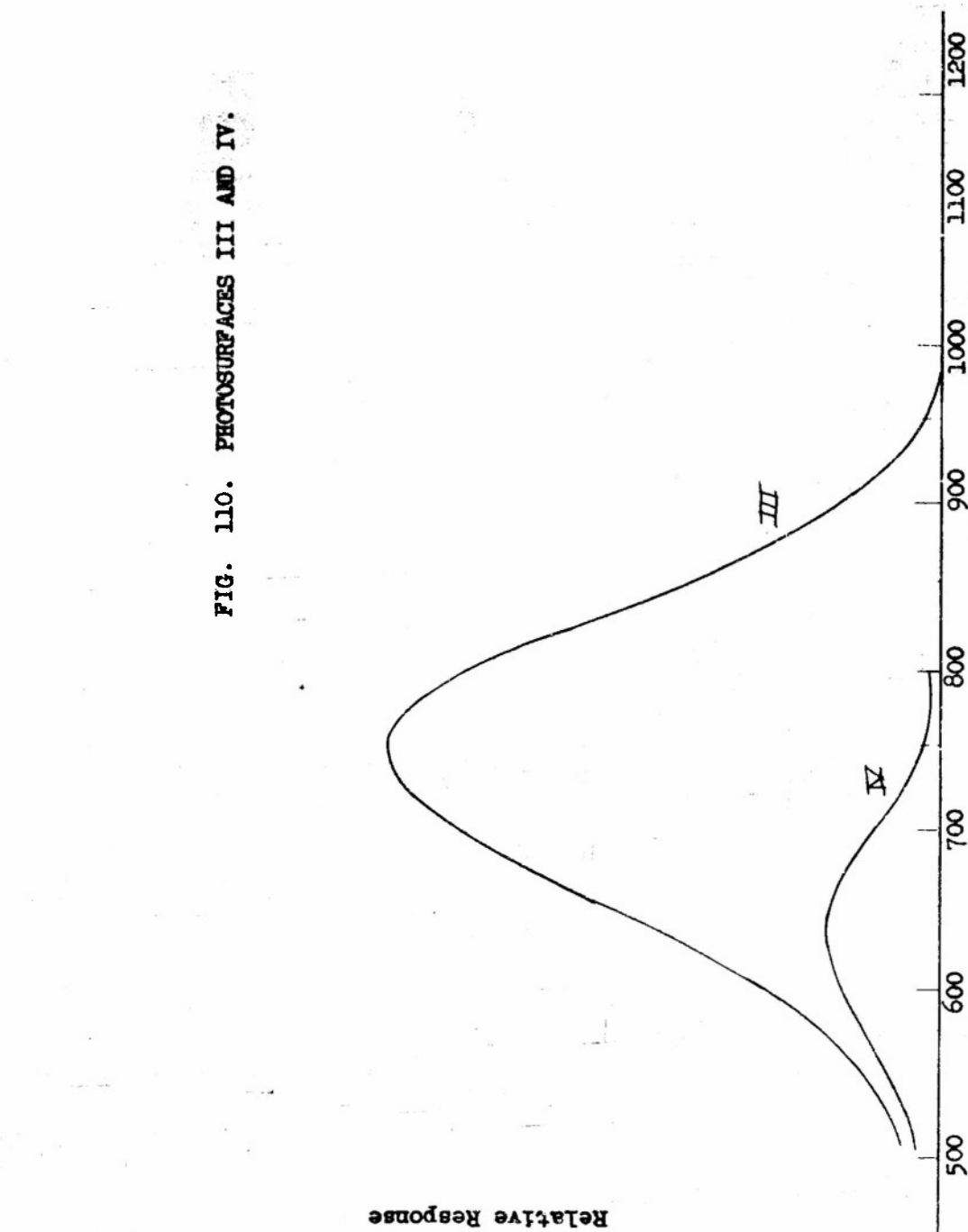
Surface	Wavelength at Maximum Photoelectric Emission	Long Wavelength Limit
II	< 940 $\text{m}\mu$	< 1350 $\text{m}\mu$
III	750 $\text{m}\mu$	~1000 $\text{m}\mu$
IV	650 $\text{m}\mu$	800 $\text{m}\mu$
V	545 $\text{m}\mu$	675 $\text{m}\mu$

The spectral response curve for photosurface II is shown in Fig. 109, while III and IV photoresponses are shown in Fig. 110.

X-ray diffraction studies of tubes, to which cesium was added until  $(\text{Cs}/\text{O})=2.8$ , indicated that the dominant phases present were  $\text{Cs}_2\text{O}$  and  $\text{Cs}_3\text{O}$  (see Section 4.21). This photosurface is characterized by a spectral response having a maximum at 650  $\text{m}\mu$  and a long  $\lambda$  limit near 800  $\text{m}\mu$ . Considering the process of forming this photosurface at 150°C it is reasonable to assume that the  $\text{Cs}_3\text{O}$  forms a surface layer. Thus photosurface IV can be considered as typical of  $\text{Cs}_3\text{O}$ .

On distillation of cesium away from the photosurface IV the response corresponding to photosurface III is quickly obtained. Further baking with the removal of excess cesium by distillation into a cold trap or reaction with the tube envelope results in the gradual production of photosurface II. A clue to the chemical change occurring in the first step above is provided by some work of Dr. Khi-Ruey Tsai on the preparation of  $\text{Cs}_2\text{O}$  by heating  $\text{Cs}_3\text{O}$ . It was found in this work that heating  $\text{Cs}_3\text{O}$  in vacuo led to the formation of a solid residue whose color was black. X-ray diffraction photographs showed that the residue was  $\text{Cs}_2\text{O}$  and the black color was presumably due to a small residue of excess cesium. Long continued heating in vacuo was necessary in order to remove this residue of excess cesium and produce the typical pale orange-yellow crystals of  $\text{Cs}_2\text{O}$ . The significant fact for the present discussion is that the last trace of excess cesium is difficult to remove. Extended heating in vacuo is required. This suggests that photosurface III is associated with the formation of  $\text{Cs}_2\text{O}$  containing a slight excess of cesium. This seems to accord with the observed fact that the addition of a small amount of cesium to an infrared-sensitive cathode at room temperature results in a photosurface III response. To shift the response to IV requires a considerably larger

FIG. 110. PHOTOSURFACES III AND IV.



excess of cesium.

As stated above, photosurface III can be converted to II by means of extended baking, at 130 - 150°C, provided that a cold trap, or something similar, is present to adsorb the cesium distilled from the cathode. To convert this photosurface to the good infrared surface I it is necessary to have a good cesium getter in the phototube. In the case of tubes which did not contain appreciable amounts of the white solid formed during tube envelope seal off it was very difficult to proceed from curve II to I. It was, however, possible to recover the infrared response I by selectively flaming the tube envelope while maintaining the cathode at approximately 190°C. This process presumably resulted in the recovery of the infrared response by reacting the excess cesium at the hot tube wall. In view of these observations it seems likely that in going from photosurface III to II to I only a relatively small amount of cesium need be removed. This small amount is, however, difficult to remove and it becomes progressively more difficult to remove it as the reaction proceeds.

In the case of the cesium deficient 150°C tubes ( $Cs/O \sim 1.5$ ) no new types of response curves are observed. Frequently, however, it is observed that the contribution of the IA response is smaller than the IB thus producing two maxima in the spectral response for such a tube.

It is interesting to note that spectral response IB is very similar to III. The above observation that IB is favored over IA in cesium deficient tubes seems at first sight to suggest that IB and III arise from different emitting centers despite the apparent similarity in shape. For response III is definitely associated with a small excess of cesium in  $Cs_2O$  while IB, being favored in cesium deficient tubes, is apparently associated with a deficiency of cesium. There is, however, another possibility. That is, that the centers giving rise to response IA are very sensitive to small variations in cesium content either above or below some optimum amount. The fact that response IA is sensitive to small excesses of cesium seems established conclusively. That it is sensitive to cesium deficiency is less well established but is compatible with the data. This has already been indicated by the data of Section 3.2 which shows that the contribution of the IA response is reduced relative to IB on extended baking (see e.g. curves 6, 7, 8 of Fig. 29). However, even more extensive baking also affects the contribution of the IB response (see curves 9, 10, 11, 12 of Fig. 29). The idea that the centers of type IA are more sensitive to small excesses or deficiencies of cesium than are the



centers of type IB is a very attractive one which would account for much of the experimental work which has been done on massive cathodes. It is not difficult to prepare cathodes with responses of type IB. It is more difficult to prepare cathodes with high response of type IA. Much more careful control is required.

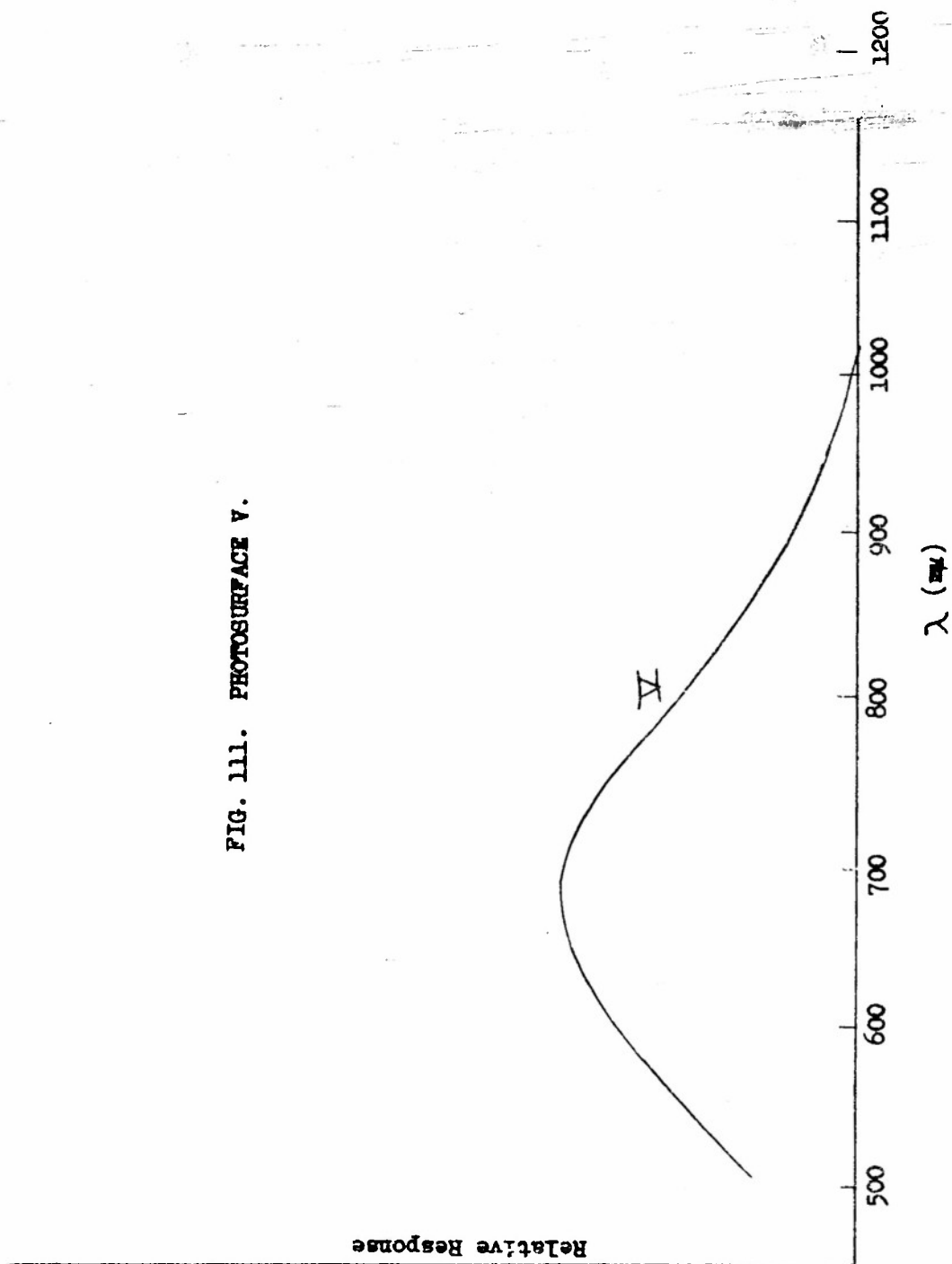
On extended baking the spectral sensitivity of a good infrared surface, I or II, decreases to spectral response V of Fig. 111. Further baking of this surface finally results in a complete loss of the visible and infrared response. As noted in Section 3.2 the composition of this surface is unknown. The nature of the chemical reactions which may occur at the surface during extended baking has not been investigated.

In the preceding discussion no attention has been paid to the role of silver in the cathode since we wish to postpone the discussion of this factor until the next section. It is to be understood, however, that silver in the cathode plays an important role and it may well be involved in all of the responses considered in the present section.

One additional, and rather special, type of photocathode is occasionally obtained which is worth noting, although it has not been possible to reproducibly prepare such cathodes. The type of spectral response involved is indicated by the results obtained for PT18C.

In Fig. 112 the spectral response of PT18C is compared to the Class I infrared surface. It is apparent that the surface has an appreciably higher sensitivity at wavelengths greater than 1200  $m\mu$  than the photosurface I. PT18C was actually prepared under rather poorly controlled conditions while mounted on the vacuum system. The  $Cs_2CrO_4$ -Si pellet was mounted within the tube envelope. After firing the pellet the tube was baked at 180 - 190°C until the thermionic emission maximum was passed. After tip off the sensitivity was low but a short bake at 130°C resulted in the stable infrared-sensitive surface. This type of infrared surface was also formed at one stage in the preparation of PT24C. The surface is characterized by a very high room temperature dark current approximately a hundred fold greater than the normal cathode. As stated earlier, we do not know how to reproducibly prepare such cathodes.

FIG. 111. PHOTOSURFACE V.



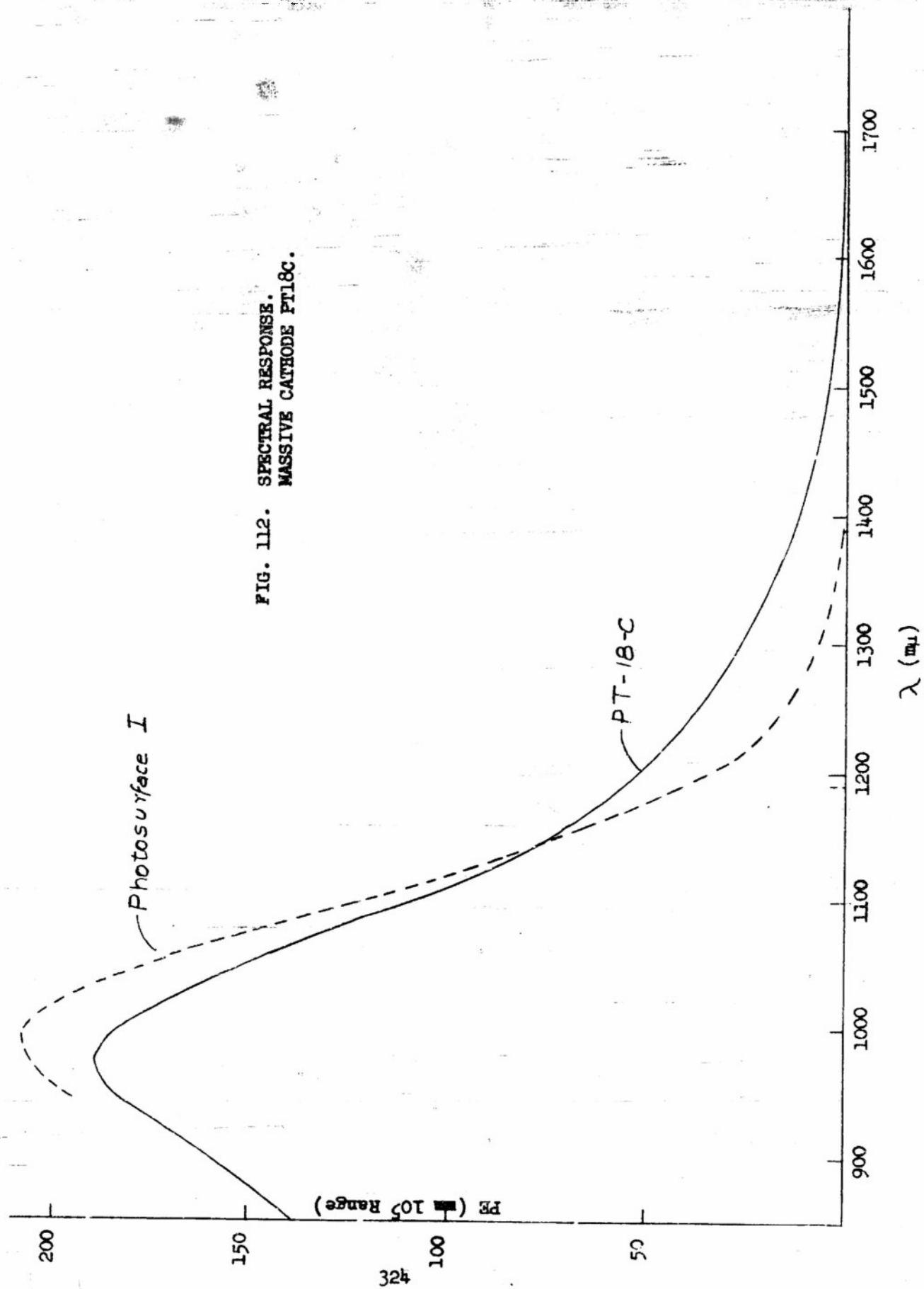


FIG. 112. SPECTRAL RESPONSE.  
MASSIVE CATHODE PT18C.

## 5. CONCLUSION. SUGGESTIONS FOR FURTHER WORK.

The results of the experimental work performed under the present contract are presented in full detail in preceding sections. In the present section the connection between the present work and previous work is pointed out where the connection is understood. Some brief comments on the present status of the theory of photoelectric emission are also made and a few suggestions for future work are made. No complete summary of work under the present contract is attempted.

The chemical constitution of photocathodes is now understood much better as the result of the present investigation. Our conclusion that  $\text{Cs}_2\text{O}$  is an essential ingredient of an infrared-sensitive photocathode agrees with the previous conclusions of Campbell<sup>20</sup>, Sayama<sup>21</sup>, and Prescott and Kelly<sup>18</sup>. The conclusion of Campbell, and Sayama, that maximum thermionic emission is obtained when the cathode (Cs/O) ratio is equal to 2 is not, however, confirmed in the present investigation. Using three different photocell designs we have found that maximum thermionic emission is obtained at three different (Cs/O) ratios for the photocell, i.e. no. of atoms of cesium entering the cell (but not necessarily ending on the cathode) to no. of atoms oxygen on cathode. The differences are undoubtedly due to the proportion of cesium on the tube walls relative to the cathode. When the cesium source is so placed that cesium atoms strike the cathode first, then the proportion on the wall is no doubt reduced and the (Cs/O) ratio for the cell is more nearly equal to that for the cathode. It seems doubtful, however, that cesium can be entirely kept off the wall by such a procedure despite the high collision efficiency and hence methods which depend on the measurement of the amount of cesium entering a photocell cannot accurately provide the (Cs/O) ratio for the cathode. The cathode (Cs/O) ratio, found in the present work by using a radioactive cesium tracer, is considerably less than 2 for tubes prepared to maximum thermionic emission. Because of the sensitivity to tube geometry it seems likely that the cathode (Cs/O) ratio at maximum thermionic emission will vary from one experimental arrangement to another. The experimental results strongly suggest that these cathodes contain more than one oxide of cesium. The oxide  $\text{Cs}_2\text{O}$  has been conclusively identified by x-ray diffraction but the other oxide has not been definitely identified. It is tentatively suggested that  $\text{Cs}_2\text{O}_3$  is the other constituent in cathodes prepared to maximum thermionic emission.

Extensive experiments have been performed to study the effect on infrared sensitivity of variations in (Cs/O) ratio. These experiments suggest that chemical equilibrium is established in cathodes which are prepared by the slow addition of cesium to oxidized silver. During the addition of cesium the cathode reactions are slow but when the cesium flow is stopped the cathode approaches within a few minutes (at 190°C) to a steady state in which thermionic emission and photocurrent become constant. This is interpreted as meaning that equilibrium is established in the cathode between  $\text{Cs}_2\text{O}$  and  $\text{Cs}_2\text{O}_3$ . Cathodes prepared in this way have high integral and infrared sensitivities comparable with good commercially available cathodes. If small amounts of excess cesium are added to such cathodes at room temperature, where reaction rate is negligibly slow, infrared sensitivity is greatly reduced. This is no doubt due to an adsorbed cesium layer. On warming the tube to a low temperature (130 to 150°C) for a few minutes infrared sensitivity is restored. This is interpreted as due to the fact that  $\text{Cs}_2\text{O}_3$  reacts with the adsorbed cesium layer thus converting it to  $\text{Cs}_2\text{O}$ . It appears that equilibrium is re-established. It has not been verified that equilibrium approached from the opposite direction, by first adding oxygen to the cathode and then heating, will restore infrared sensitivity. In speaking of a cathode "equilibrium" some caution must be exercised. Due to the extreme reactivity of cesium a slow reaction of cesium with the glass envelope of a photocell takes place at the higher temperatures. Extended baking at high temperatures may, and usually does, cause further changes to occur in cathode sensitivity. These are regarded as due to the fact that cesium content of the cathode undergoes further changes as the photocell approaches equilibrium with the tube envelope. The interpretation is not completely clear-cut because long baking times are required and we cannot tell what might be distilled from a tube envelope on long heating even though the envelope was originally outgassed at a much higher temperature.

The above discussion indicates that high infrared sensitivity can be obtained in a cathode which might reasonably be expected to be at equilibrium. High sensitivity can also be obtained, however, in cathodes which are certainly not at equilibrium. A considerable number of cathodes have been prepared to maximum thermionic emission under conditions in which cesium is rapidly added. When the cesium flow is halted the thermionic

emission rapidly rises and then begins to decrease. If the tube is cooled to room temperature just beyond this second maximum, thus stopping further cathode reaction, then the cathodes prove to be infrared-sensitive. If, however, these tubes are baked even at rather low temperatures the infrared sensitivity may at first rise somewhat, due to further reaction which adjusts cesium content to its optimum value, but rather soon the sensitivity begins to decrease and this continues until infrared sensitivity is entirely lost. It has been suggested that these cathodes contain unreduced silver oxide and establishing equilibrium in this case leads to a poor tube. It seems probable that many commercial cathodes are of this type. Considerable care must be exercised in baking such cathodes. From these experiments it is entirely clear that equilibrium is not essential to high infrared sensitivity. The results have been interpreted as meaning that the presence of  $\text{Cs}_2\text{O}$  in a cathode is not enough to insure high infrared sensitivity. A small quantity of cesium is also important. This small quantity must be adjusted to its optimum concentration. It must be emphasized that it is not known whether the optimum content of cesium in  $\text{Cs}_2\text{O}$  is in excess of the stoichiometric ratio of two cesium atoms to one oxygen. The optimum might be above, equal to, or below the stoichiometric ratio. It is known, however, that the amount of cesium involved is very small compared to the total cesium in chemical combination in the cathode. In speaking, therefore, of an "optimum cesium content" it must be recognized that the question of whether  $\text{Cs}_2\text{O}$  in the cathode is a stoichiometric compound is left open. Since x-ray diffraction lines from the sensitive layer of the cathode correspond well with those of bulk samples of  $\text{Cs}_2\text{O}$  containing less than 0.1% of excess cesium it follows that the (Cs/O) ratio must be nearly 2. Very small departures from this ratio might, however, markedly affect photoelectric emission.

It was shown during the course of the radioactive cesium tracer study that a volatile oxide of cesium is formed when the cesium to oxygen ratio for the cathode exceeds 2. This may be important in cases where photocathodes are prepared by first adding large excesses of cesium and then distilling the excess from the cathode. In such a process oxygen as well as cesium is transported from the cathode. It is interesting that Campbell<sup>20</sup> came to the same conclusion during an early stage of his investigation but later changed his mind. His first conclusion was the correct one.

It appears that the simple idea that infrared sensitivity is associated with  $\text{Cs}_2\text{O}$  in the cathode and with an "optimum cesium content" is sufficient, when account is taken of reaction with the tube wall and slowness of the cathode reactions, to correlate the various observations which have been made on massive cathodes. The chemical behavior of such cathodes is at least qualitatively clear. When, however, alterations are made in the silver base on which cathodes are prepared a new factor makes itself felt. Conclusive evidence has been obtained that the silver base markedly affects the final cathode. It seems probable that the effect occurs at the oxidation step but the precise nature of the factor involved is not known. From the discussion of previous work given in Section 1 it seems definitely established that silver has a pronounced effect on infrared sensitivity. The silver referred to is apparently that which is finely dispersed through the cathode, although perhaps not an atomic dispersion (i.e. solid solution). Such finely dispersed silver may be produced by the reaction of silver oxide with cesium or by evaporation onto a cathode followed by heating as in the case of Asao's work<sup>23</sup>. It is known that the silver oxide produced during the glow discharge oxidation of silver is not purely  $\text{Ag}_2\text{O}$ . Other, more highly oxidized oxides, are also produced in considerable proportions. The composition of the silver oxides produced is no doubt sensitive to processing conditions including the condition of the silver base. The proportion of "precipitated" silver, obtained by reaction of silver oxide with cesium, which appears in the final cathode is of some interest. Extreme limits can be set by considering two alternative cases. In the first case we assume that the oxide formed is  $\text{Ag}_2\text{O}$ . Then on complete reaction with cesium to produce Ag and  $\text{Cs}_2\text{O}$  a cathode would be produced containing 26% by volume of precipitated silver (ignoring voids). If, on the other hand, the oxide produced is  $\text{Ag}_2\text{O}_3$  (the most highly oxidized oxide known) then after cesium addition precipitated silver would constitute 10% by volume. The actual volume percent of silver in the final cathode probably lies somewhere between these extremes. It seems quite possible that variation between these limits would have considerable effect on infrared sensitivity. In order to fully characterize the cathode it would be necessary to measure the amount of precipitated silver in the cathode and to obtain some estimate of particle size. We have not been able thus far to devise any means for achieving this objective although its importance is obvious. In order to successfully perform such measurements it would apparently be necessary to further develop the chemistry of the silver



oxygen system. This would require a great deal of preliminary chemical investigation not related to cathode preparation. The problems involved are undoubtedly extremely difficult and tedious. We have not attempted to fully explore this area since the time involved would be excessive. In view, however, of the results which have been obtained we must accept the view that the presence of  $\text{Cs}_2\text{O}$  with optimum cesium content is not in itself enough to insure high infrared sensitivity. From the work reviewed in Section 1 it appears that finely dispersed silver in proper proportion is also essential and other, as yet unrecognized factors, may also be involved.

The preceding discussion has, to some extent, related the composition study of the present report to the researches of previous workers. There remains some comment concerning the comparison of the spectral responses obtained here with those of previous workers. We have previously pointed out on several occasions that the spectral responses obtained in our work seem, for highly infrared-sensitive cathodes, to be representable as the superposition of two spectral response curves and thus two different types of emitting centers are suggested. One of these has a maximum at about  $750\text{ m}\mu$  and the other at about  $950\text{ m}\mu$ , the latter being sensitive to small variations in cesium content. When the spectral response curves are roughly corrected for dispersion and lamp energy distribution, as in Section 3.2, the shape of the response with its maximum at  $750\text{ m}\mu$  becomes closely similar to several of the response curves obtained by the investigators listed in Table IV of Section 1.9. The correction for dispersion and lamp energy distribution is rough but it seems adequate to justify at least the tentative proposal that the spectral response is equivalent to those obtained by several investigators listed in Table IV. The (uncorrected) response referred to is curve IB of Fig. 108. There is some reason to think that this identification may be correct. Prescott and Kelly<sup>18</sup>, for example, reported that their cathodes contained excess cesium. We would expect, if the excess is not too large, that a response curve of type IB would result. Asao<sup>23</sup> also reported a considerable excess of cesium. Under these conditions a response of type IB, or even IV (Fig. 110) if the excess is high enough, might be expected. In other cases the composition is not reported. These considerations suggest that the investigators of Table IV are studying the behavior of only one of the two

types of emitting centers which are involved in infrared-sensitive cathodes. Investigation of optical properties of cathodes, reported in Section 1, always involve the preparation of specular reflecting cathodes and under these conditions centers of type IB seem to result, at least in the work listed in Table IV. It would appear, therefore, that most of the investigations discussed in Section 1 are concerned with emitting centers of type IB. Thus centers of type IB give rise to a volume photoelectric effect rather than a surface photoelectric effect etc. as described in Section 1. We might well ask, therefore, whether centers of type IA (Fig. 108) also give rise to a volume photoelectric effect. The answer here is not definitely known. The difficulty involved in the study of centers of type IA are very clearly illustrated by the work of Kluge<sup>26</sup>. He showed that much more highly infrared-sensitive cathodes could be obtained on rough silver bases than on specular reflecting silver bases. These highly infrared-sensitive cathodes are not, however, specular reflectors and hence the techniques of Section 1.6 cannot be applied in a test of volume vs. surface photoelectric effect. This greatly complicates matters so that a definite statement is not possible at this time. It has been demonstrated that photoelectric emission by centers of type IA is suppressed almost completely by the addition of very small quantities of cesium at room temperature (see Section 3.41). This suggests at least a surface sensitive component. However, it has also been shown that reducing the extent of oxidation (and hence forming a thinner cathode) reduces the contribution of centers of both types IA and IB. Thus the volume of sensitive material is important. This does not conclusively show that a volume photoelectric effect is involved. For two cathodes of different thickness do not necessarily contain particles of the same size. On the other hand, this observation certainly must be accounted for before any proposal can be accepted which regards centers of type IA as leading to a surface photoelectric effect. In fact, we doubt that a surface photoelectric effect is involved, although a definitive proof is lacking. The effect of small amounts of excess cesium may be due largely to alteration in work function although again, this is not proven. Due to the extreme sensitivity of centers of type IA it is difficult to perform definitive experiments. It must finally be stated that, despite Kluge's work, it is not established that cathodes containing centers of type IA are necessarily non-specular reflectors. One of the most sensitive commercial cathodes which we have ever

tested, a "lighthouse" tube of British manufacture, was semitransparent and seemed on superficial examination to be specular.

It seems worthwhile at this point to comment briefly on the effect on photocathodes produced by impurities introduced through the vacuum system. A vacuum system has been used in cathode preparation in which a mercury diffusion pump and an efficient cold trap was employed (tracer experiments). Another vacuum system has also been used in which an efficient (three stage) oil diffusion pump was employed without a cold trap. Cathodes prepared under comparable conditions in these two systems had comparable infrared sensitivity. All kinds of difficulties have been encountered in the preparation of photocathodes but none of these could even be traced to the effect of impurities from the vacuum pumps. Slight amounts of such impurities must, however, have been present. It is believed that the cathodes were not sensitive to such impurities for the following reason. The photocathodes studied here contain considerable quantities of sensitive material. Moreover, a volume photoelectric effect is involved certainly with one type of emitting center and perhaps with the other. Impurities from vacuum pumps are serious in the study of phenomena which are affected by amounts of impurity of the order of a monolayer or a fraction of a monolayer. The present cathodes are no doubt sensitive to amounts of impurity of the order of a monolayer at room temperature where chemical reaction takes place at a negligible rate. When heated, however, to moderate temperatures (130 to 190°C) the reaction rates become faster. Thus the effect of a small amount of surface impurity is overcome by the shift in equilibrium which occurs at the higher temperatures. The surface is thus restored by chemical reaction to its original condition (or nearly so) at least insofar as factors governing infrared sensitivity are concerned. This applies, of course, only to equilibrium cathodes originally prepared by slow addition of cesium. It may also apply to other cathodes, however, if the baking temperature is not too high. It must be emphasized that a sloppy vacuum technique cannot be tolerated and was certainly not used in our work. Excessive precautions beyond those discussed in Section 2 are, however, apparently unnecessary in this work except, perhaps, under unusual conditions in which the cold photocell remains attached to the vacuum line. In conclusion it must be stated that Octoil-S was used in the oil diffusion pump. The situation outlined above might not prevail if a silicone oil were used.

We must now consider briefly the status of theories of the photoelectric effect in silver-oxygen-cesium photocathodes. The original theory of de Boer is still accepted by many investigators<sup>49</sup>, although evidence has accumulated which casts doubt on its general applicability. According to de Boer's theory (see Section 1.4) the source of photoelectrons is an adsorbed layer of cesium atoms on  $\text{Cs}_2\text{O}$ . The cesium atoms which are most strongly bound (at "active spots" on the surface) contribute to photosensitivity furthest in the infrared. If too large an amount of excess cesium is added, so that multi-layers of cesium collect on the surface, then infrared sensitivity declines because the photoelectrons then originate in essentially metallic cesium which is known to have low sensitivity in the far infrared. According to de Boer silver, or some other metal, must be mixed with a thick "intermediate layer" ( $\text{Cs}_2\text{O}$ ) in order to provide electrical conductivity so that external photoelectrons can be replaced from the base metal. On the basis of this theory  $\text{Cs}_2\text{O}$  containing finely dispersed silver and a small optimum amount of excess cesium are required for high sensitivity. At first sight this seems to agree very well indeed with the conditions which we outlined above. However, this theory seems to require a surface photoelectric effect and this does not agree with an accumulation of data which indicate a volume photoelectric effect. Thus the relative importance of the mechanism proposed by de Boer is open to question. The proposal is a plausible one on theoretical grounds and seems to account for a low work function. It seems quite likely that some contribution to the photocurrent must be made through de Boer's mechanism. There is considerable doubt, however, that this contribution is the major one. In Sayama's theory of the photoelectric effect<sup>51</sup> the source of photoelectrons is assumed to be the finely dispersed silver in the cathode. Sayama's argument is quite rough at best and seems to be weakened by the work of Borziak<sup>1</sup> who determined the optical constants for the cathode. The situation is, therefore, in confusion. A major objection to de Boer's theory would be removed if some modification could be found which provided for a volume photoelectric effect. This would not, however, completely remedy the situation as long as photoelectrons originate from cesium atoms distributed through  $\text{Cs}_2\text{O}$  since we would be hard pressed to account for the fact that  $\text{Cs}_2\text{O}$  (without silver) is not sensitive in the far infrared. Photosensitivity at shorter wavelengths might be accounted for in this way but not at longer wavelengths. We find it hard to believe that poor electrical conductivity could completely account for the difference. Some further modification

which directly involves silver in photoelectron production would be an improvement since, thereby, many of the desirable features of Sayama's theory could be rescued. During the course of preparing this report such a modification of de Boer's theory has suggested itself. The conception came too late to permit a quantitative development of its consequences so it can only be briefly outlined as a highly tentative proposal which seems at least to justify further and more quantitative theoretical consideration.

This proposal is based on de Boer's observation that a dielectric layer tends to take up alkali metal (including cesium), on heating in the vapor, much more easily when foreign metal atoms are already present in the dielectric layer (Ref. 22 p. 322). This is attributed by de Boer to the fact that the presence of finely dispersed metal in the intermediate layer ( $\text{Cs}_2\text{O}$ ) results in disruption of the structure so that internal cracks etc. are available at which cesium atoms may be internally adsorbed. This may, however, be accounted for in another quite different way. In order to see how this comes about let us consider the various steps which might reasonably occur on adding cesium to  $\text{Cs}_2\text{O}$  containing finely dispersed silver. The work function for silver is greater than the ionization potential for cesium. Hence it seems reasonable that electrons will tend to be transferred from cesium to silver. This leaves an adsorbed layer of cesium ions on the surface and charged silver particles on the interior. Since electron mobilities are high this charge transfer must be fast. An electric field is thus established which favors the forced diffusion of ions in the lattice of  $\text{Cs}_2\text{O}$  so that oxide ions tend to diffuse to the surface or cesium ions move to the interior, or both. This diffusion is favored by high temperatures, of course. When equilibrium is re-established the surface charge will have been at least partially neutralized the overall effect being that cesium ions have moved into the interior of the  $\text{Cs}_2\text{O}$  crystal. There is now an excess of cesium ions on the interior of the crystal and these ions must either occupy sites of the lattice at which there are ion deficiencies or they must occupy interstitial positions. The degree to which cesium ions penetrate the lattice will depend on the availability of positions which they can occupy without excessive distortion of the lattice. The lattice of  $\text{Cs}_2\text{O}$  is, however, well supplied with interstitial positions which lend themselves to such occupancy. Crystalline  $\text{Cs}_2\text{O}$  has a layer type lattice (see Part III of this Final Report Series). Each layer can be regarded as a sort of sandwich in which a sheet of oxide ions is included between two



sheets of cesium ions. Each layer is ideally electrically neutral. These layers are stacked together to form the crystal. Adhesion between layers is not high as indicated by the shearing disorder observed in the x-ray investigation of  $\text{Cs}_2\text{O}$  (see Part III). This has been further verified by calculating the Coulomb interaction between layers. Moreover, the minimum distance between two cesium ions in adjacent layers is substantially greater than twice the ionic radius of cesium. Thus the layers are not very closely packed. The interstices between layers could be occupied by cesium ions without major lattice distortion. Hence it seems very likely that diffusion of cesium ions into the interior of  $\text{Cs}_2\text{O}$  can take place to a considerable extent. Thus at equilibrium we visualize the cathode interior as containing charged colloidal silver particles and extra cesium ions distributed through the lattice in sufficient numbers to make the whole system electrically neutral. The situation is somewhat similar to that which prevails in a colloidal dispersion in an aqueous electrolytic solution. This picture would account in a very satisfactory way for de Boer's observation that intermediate layers containing dispersed metal take up cesium more easily than those without dispersed metal. Now, however, the electrons are attached to silver and the mechanism for photoelectric emission involves the ejection of electrons from charged silver particles. Considered in a purely qualitative light this view has much to recommend it. In the first place it probably describes the internal situation in a cathode more accurately than does de Boer's model. In the second place it involves silver explicitly in the mechanism of photoelectron production. In the third place it accounts for the fact that excess cesium is taken up largely because silver is present. It is hard to account for excess cesium in the cathode under the conditions of preparation if we assume that only pure  $\text{Cs}_2\text{O}$  is involved. For experiments on bulk  $\text{Cs}_2\text{O}$  (without silver) have shown that it retains only very slight excesses of cesium when prepared under conditions approximating cathode preparation. With finely dispersed silver present, however, it no doubt retains more than in the absence of silver. In the fourth place a volume photoelectric effect is accounted for. Or at least a volume photoelectric effect is simulated since the charged silver particles are distributed throughout the cathode. Actually the ejection of electrons from a particular silver particle involves a surface photoelectric effect but the "surface" involved is the silver- $\text{Cs}_2\text{O}$  interface and not the geometrical area of the cathode. Finally, this theory must, in order to be successful, provide for a low work function, i.e. the minimum change in energy accompanying the ejection of an electron without residual kinetic energy.

That such can be the case is best illustrated by a thermodynamic argument. In de Boer's theory photoelectrons are ejected from strongly adsorbed surface cesium atoms. Let us suppose that cesium is added to a cathode until the interior becomes saturated so that the addition of further cesium results in adsorbed cesium atoms which do not lose their electrons to the interior. We then have equilibrium established, i.e. further transfer of electrons increases the free energy. Hence the free energies, or more accurately the chemical potentials, of the electrons in metallic silver (charged) and adsorbed cesium atoms must be equal since otherwise equilibrium could not be established. The free energies for electrons differ from the energies by an amount equal to the absolute temperature times the entropy. But the entropy of electrons in a metal at room temperature is very nearly zero. Hence the electron energies, as well as free energies, for adsorbed cesium atoms and charged silver particles are very nearly equal. Once this condition has been achieved the energy change accompanying the removal of electrons from adsorbed cesium atoms must be nearly equal to the energy change accompanying the removal of electrons from the charged silver particles. If, therefore, de Boer's theory predicts a low work function for the ejection of electrons from adsorbed cesium atoms, which it does in a clear and convincing manner, then the work function for the ejection of electrons from the charged silver particles in equilibrium with adsorbed cesium atoms must be equally low. By means of this simple argument it becomes clear that the chief virtue of de Boer's theory (low work function) is retained while at the same time a volume photoelectric effect is accounted for. Moreover, since the electron ejection now comes from charged silver particles the attractive features of Sayama's theory are also retained. In order to correct Sayama's theory it is only necessary to alter the optical constants to those which have been observed in treating the interference of light within the cathode and to recognize that the rate of photoelectron production depends, not upon the rate of absorption of photons in the cathode, but only upon the rate of absorption in the charged silver particles. Since the evidence is already strong that light interference alone cannot account for the selective maximum in photoelectric yield the replacement of Sayama's optical constants by the actual ones will probably not change the fact that the selective maximum in photoelectric yield arises from light absorption in silver. The qualitative arguments given above are not by any means sufficient to establish the validity of the proposed model. They do seem sufficient, however, to indicate that the



proposal deserves further study. Possible extensions of this proposal are numerous. Electrons might be trapped at silver atoms interstitially dispersed through the cathode. We regard this as a limiting case of the "fine dispersion" referred to above. Other foreign atoms also deserve consideration. Since nothing definite can be done about these possibilities at present we shall leave the matter at this point.

Several facts concerning cathode behavior are not accounted for. In the first place no clear-cut proposal can be made as to the difference between the two types of emitting centers. Moreover, the photoelectric yield is temperature dependent. This might be due to temperature dependence of electronic mean free path since a volume photoelectric effect is involved. This involves the assumption that it is the probability of escape of an internal photoelectron which is temperature dependent. This is invoked to account for the fact that photoelectric yield increases as the temperature goes down. Other explanations might also be concocted but none can be proven. Further discussion does not seem profitable.

There remains the final matter of appraising the status of the problem and pointing out the areas where further work seems desirable. We believe that by far the most important factor to be studied is the effect of silver base on cathode properties. The most valuable type of study would be one in which some variable directly related to the presence of precipitated silver in the cathode could be continuously followed as a cathode is prepared. This will not be easy to do and we have no explicit proposal to make at this time. The quantitative determination of the amount of precipitated silver in the cathode is also of interest. This could be done if some means could be found for determining the amount of silver which reacts on oxidation. This could be done if quantitative means were developed by which the oxide formed could be removed and the amount of silver determined by analysis. This would involve, however, the destruction of the cathode and, moreover, the analytical method would require considerable investigation. The analysis could, however, unquestionably be achieved although considerable development would be required. If the chemical properties of the oxidation products and their chemical composition were better known then x-ray methods could be applied in continuously following the cathode silver oxide content, although the technique would not be easy to develop and a great deal of purely chemical preliminary work would be required. We do not know how to study the influence of

silver base in a straight forward manner. As the matter now stands the effect of silver base is of first importance but the investigation of this effect is a very difficult problem.

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NOTE: In submitting this report it is understood that all provisions of the contract between The Foundation and the Cooperator and pertaining to publicity of subject matter will be rigidly observed.

Investigator \_\_\_\_\_ Date \_\_\_\_\_

Supervisor E. N. Lassiter Date Nov. 16, 1953

For The Ohio State University Research Foundation

Executive Director Oram C. Woolpert Date 17 Nov. 1953  
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